VO Biomaterials

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Literature

"Structural Biological Materials - Design and Structure-Property Relationships", ed. M. Elices, Pergamon (2000).

"Structural Biomaterials", J. Vincent, Macmillan (1982), Princeton University Press (1990, revised edition).

"Wood – The internal optimisation of trees", C. Mattheck & H. Kubler, ed. T. E. Timell, Springer (1995).

"Biomineralization", Steve Mann, Oxford University Press (2001)

"Cats' paws and catapults - mechanical worlds of nature and people", S. Vogl, W.W. Norton & Co, New York (2000)

Table of Contents

1. Introduction

1.1 Use of biological materials

Historical applications of biological materials:

bone

construction
clothing
weapons
tools
.... etc. etc.

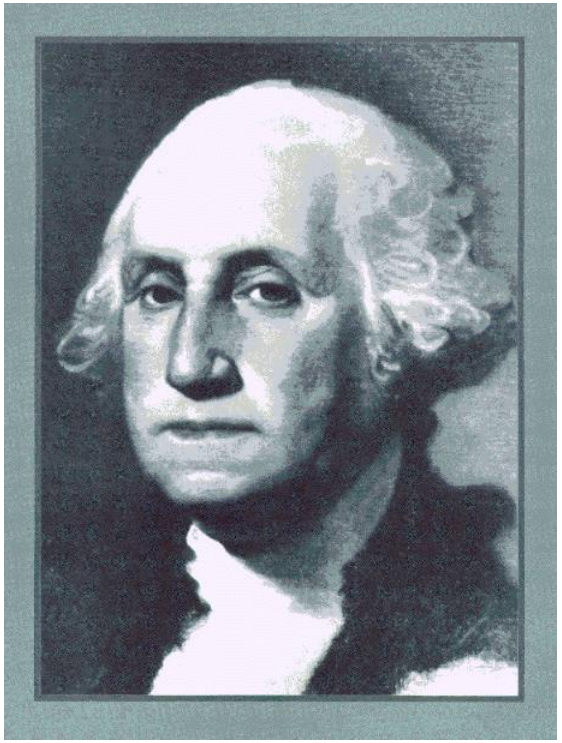
wood

1. Introduction

Biological materials for biomedical replacement:

History: biological materials were used also for prostheses and implants

George Washington's (1732-1799) teeth: made from ivory, hippopotamus bone



1. Introduction

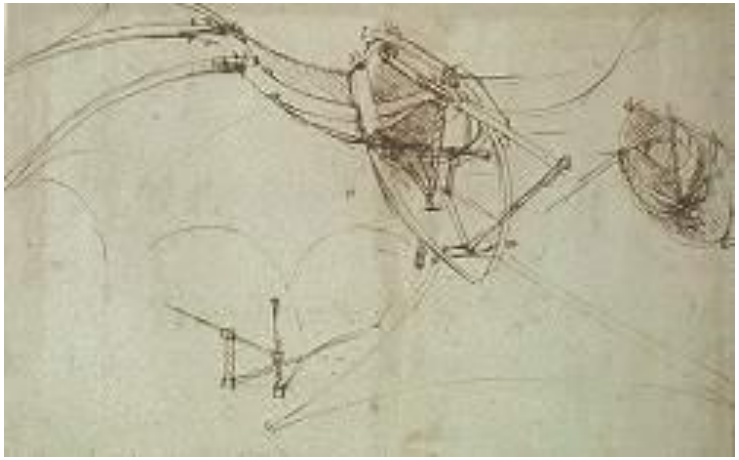
Favorable Properties of biomaterials / biostructures

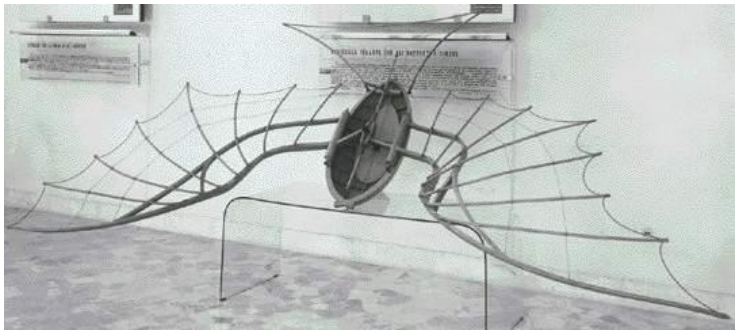
- renewable sources
- grow by themselves
- light weight (wood, bamboo)
- tough (leather)
- pleasant texture (silk)
- biodegradable

1. Introduction

1.3 Imitating Nature, examples

Pioneer of „biomimetics“: Leonardo da Vinci 1451-1519





Flying ship (ornithopter)

Small flying ship equipped with flapping wings. This is one of the most imaginative flying machines conceived by Leonardo.

The fliers' seats are located inside a shell-shaped vessel which also housed all the mechanisms (screws, nut screws and cranks) controlling the two large bat-like wings.

A particularly interesting detail is the ample plane in the tail area, most likely a system for adjusting the flying position and hence the direction of the ship itself.

Only problem: it never worked…

1. Introduction

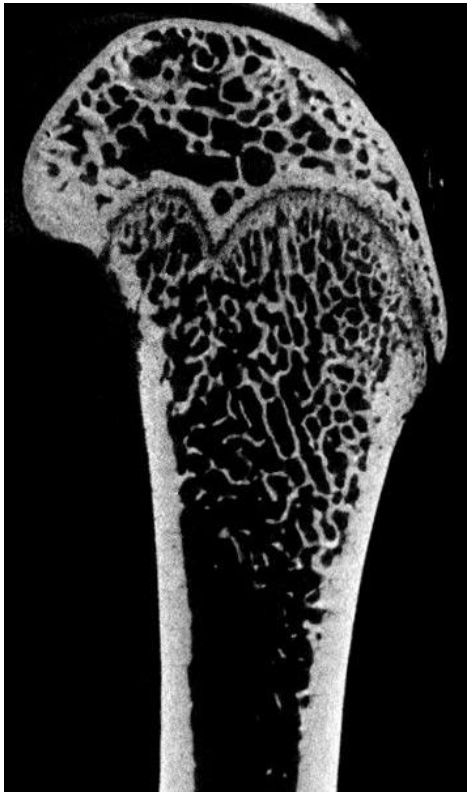
Eiffel Tower

Inspired by the architecture of the human thighbone.

Gustave Eiffel was originally fired by the work of Hermann von Meyer (professor of anatomy at Zurich) on structure of human femur, in particular the construction to carry off-center loads.

Mathematician and engineer Karl Cullman translated Von Meyer's findings into applicable theory and the mathematical model led to the design of the Paris tower.

Light-weight construction, with load carrying elements following lines of force.

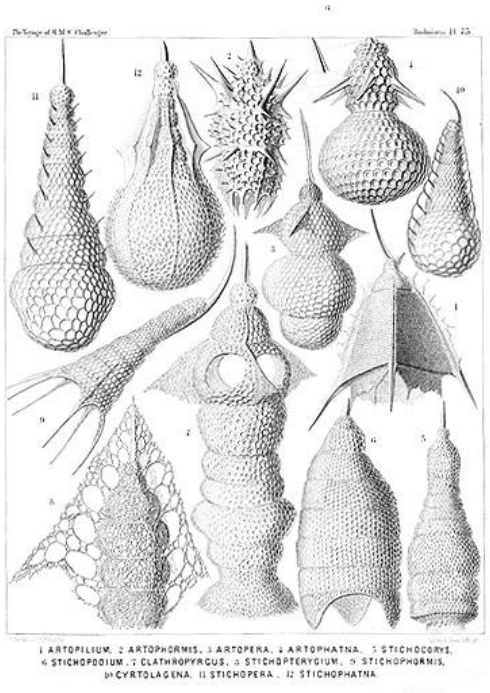


Human femur, studied by anatomist Hermann von Meyer in 1850’s

1. Introduction

Radiolarians

Unicellular algae with silica skeleton as example for architecture



Radiolarians, drawn by zoologist Ernst Haeckel (1834-1919)

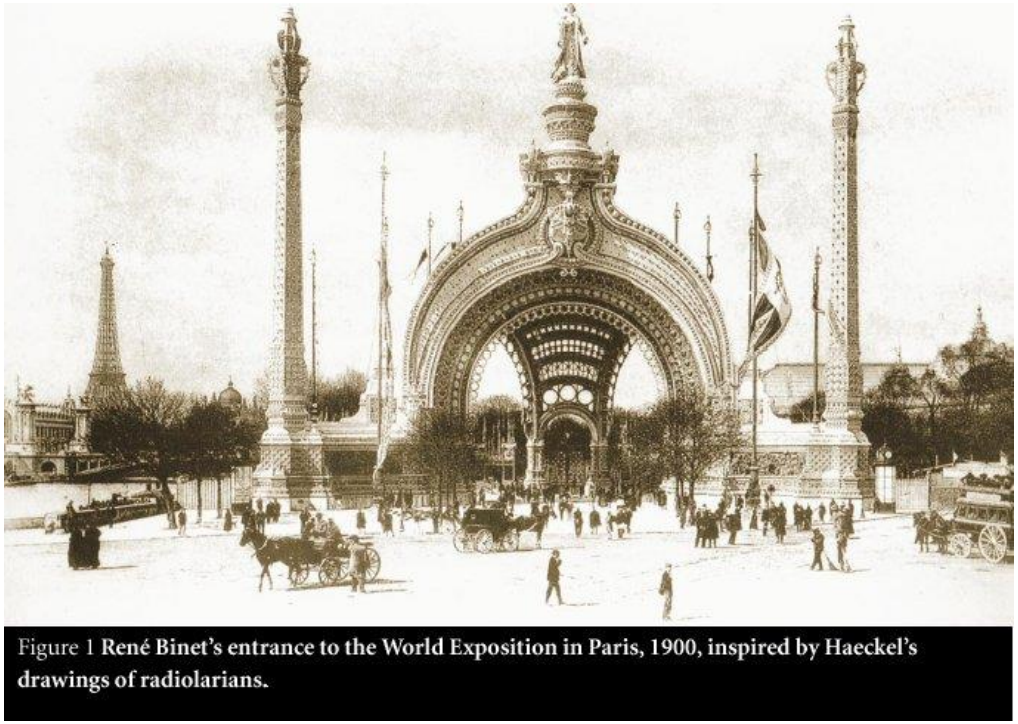


Figure 1 **René Binet's entrance to the World Exposition in Paris, 1900, inspired by Haeckel's drawings of radiolarians.**

Entrance to1900 World Exposition Paris (not existing any more)

1. Introduction

Architecture around 1900

1. Introduction

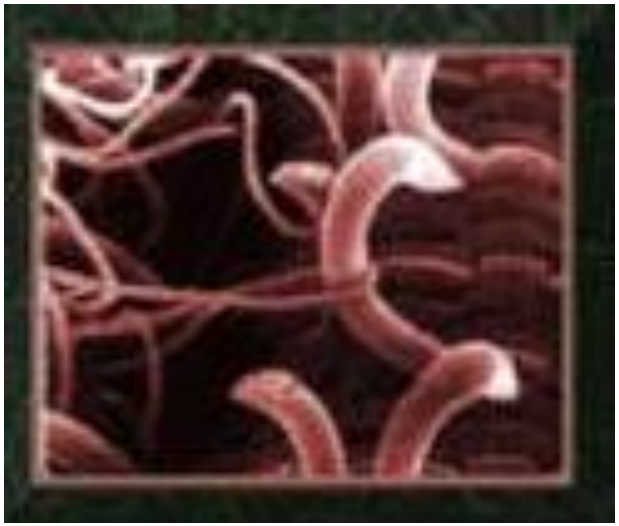
Architecture today

Kunsthaus Graz, 2003

1. Introduction

Imitating nature, examples from technology

Velcro: hook and loop fastening concept from cockleburs (patent: George de Mestral 1955)



1. Introduction

Learning from biological materials:

Natural System	**… and what it inspired (or might)**	
Red abalone shell	Building structures, composites, orthopedics, dentistry, bone repair, anti-fouling and anti-scaling agents	
Capture threads of spiders	Materials, buildings, fabrics that can absorb impact.	

http://www.asknature.org

1. Introduction

What is special about biological materials?

Nature as a designer

Nature

Human technology

1. Introduction

1.4 Construction principles in biological materials

Economic considerations

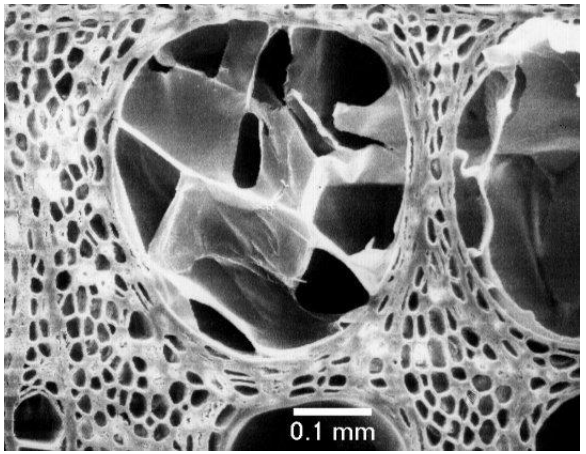
metabolically ***cheap***	relatively easy to synthesize same material – different structure
multifunctional	same tissue has different functions: e.g. bone: support and calcium storage
adaptive ‚***intelligent***‘	when conditions change, adaptation instead of exchange of parts
no maintenance	failure-tolerant structures, self-repairing
light weight	use as little material as possible

1. Introduction

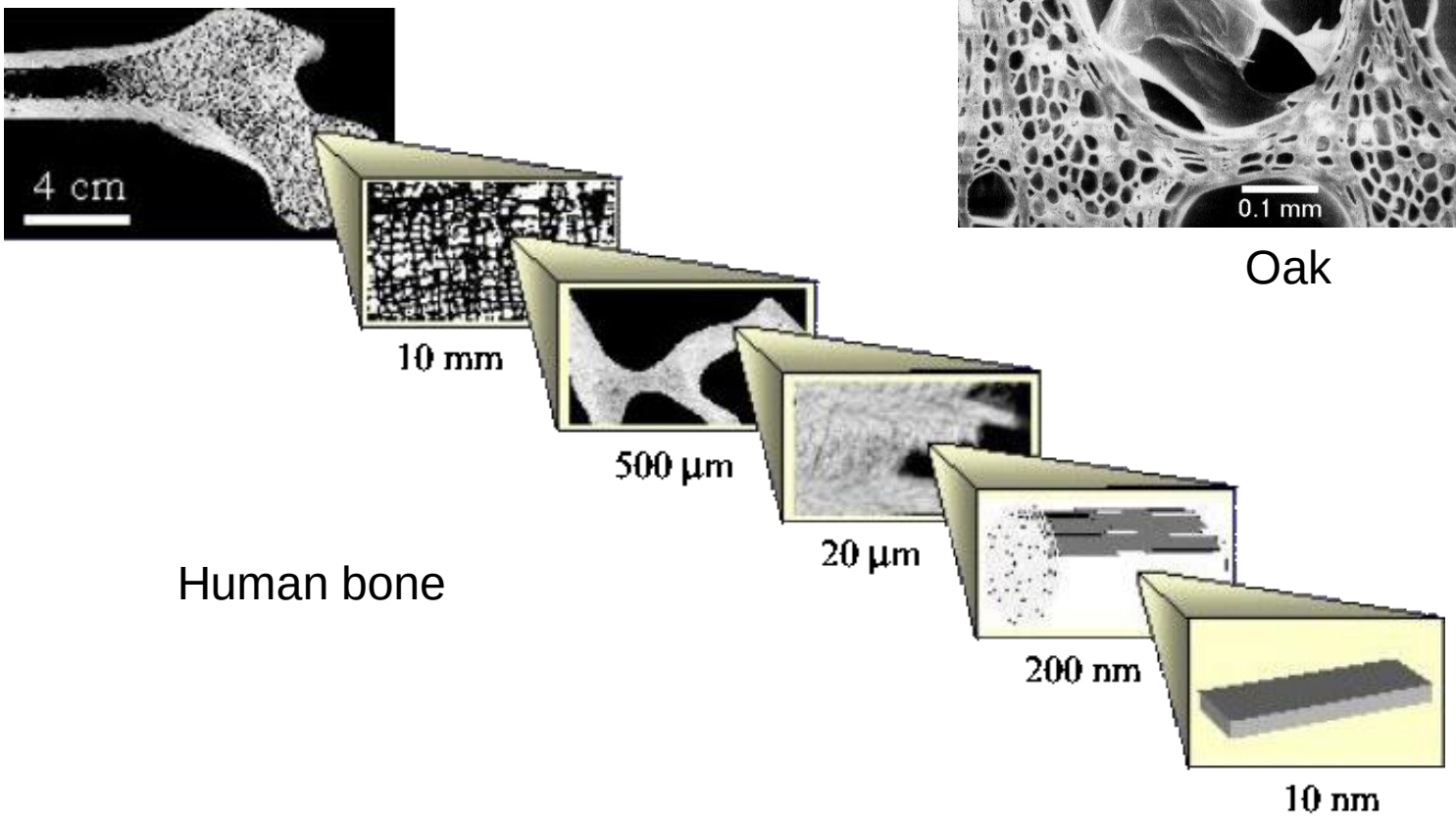
Strategies to meet economical considerations

e.g. light weight structures

Cellular, hierarchically structured



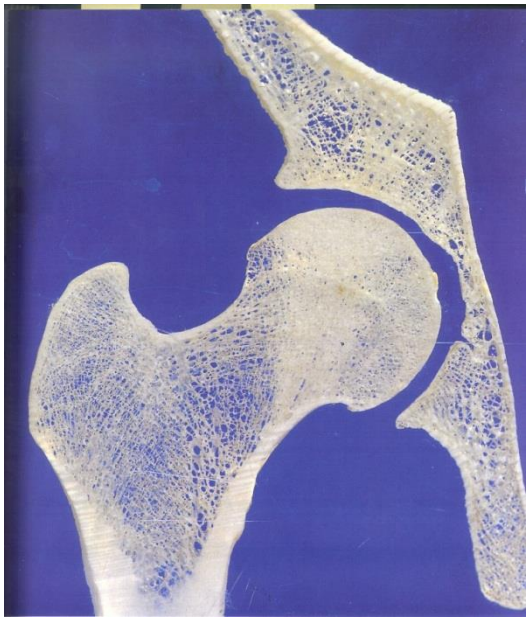
Oak

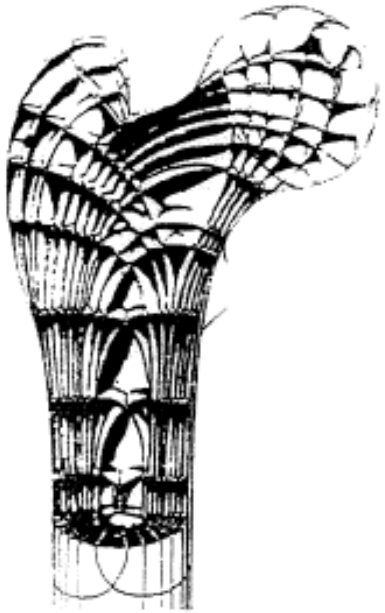


Human bone

1. Introduction

Mechanical optimization, Wolff‘s law





Courtesy of Prof. H. Zippel, Berlin

Julius Wolff (1836-1902)
German anatomist

Wolff (1892): „Form follows function“ (Wolff’s law)

•Bone has the ability to adapt, by changing its size, shape, and structure, to the mechanical demands placed on it.

•Bone is laid down where needed and resorbed where not needed.

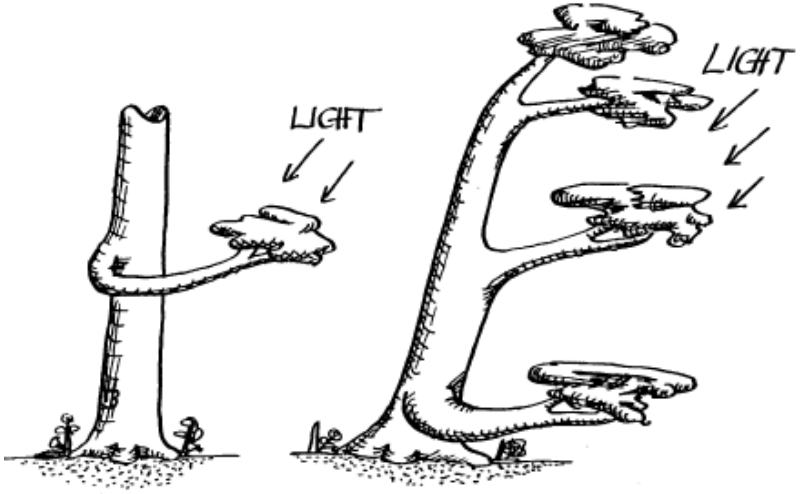
•The remodeling may be either external (a change in the external shape of the bone) or internal (a change in the porosity, mineral content, and density of bone).

D‘Arcy Thomas „On Growth and Form“ 1952

1. Introduction

Adaptive growth

Helps to keep material use to a minimum, start structure need not be ideal for later use .



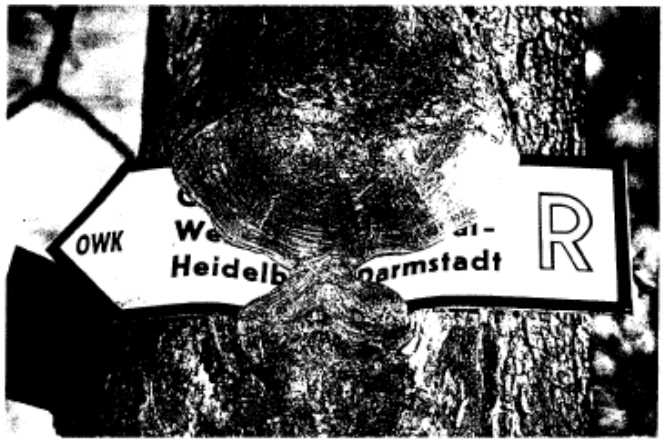


Abb. 68: Ein fest verschraubtes oder angenageltes Verkehrszeichen blockiert den alljährlichen Zuwachs und wird dabei umwallt und integriert (Foto: Frank Dietrich).

1. Introduction

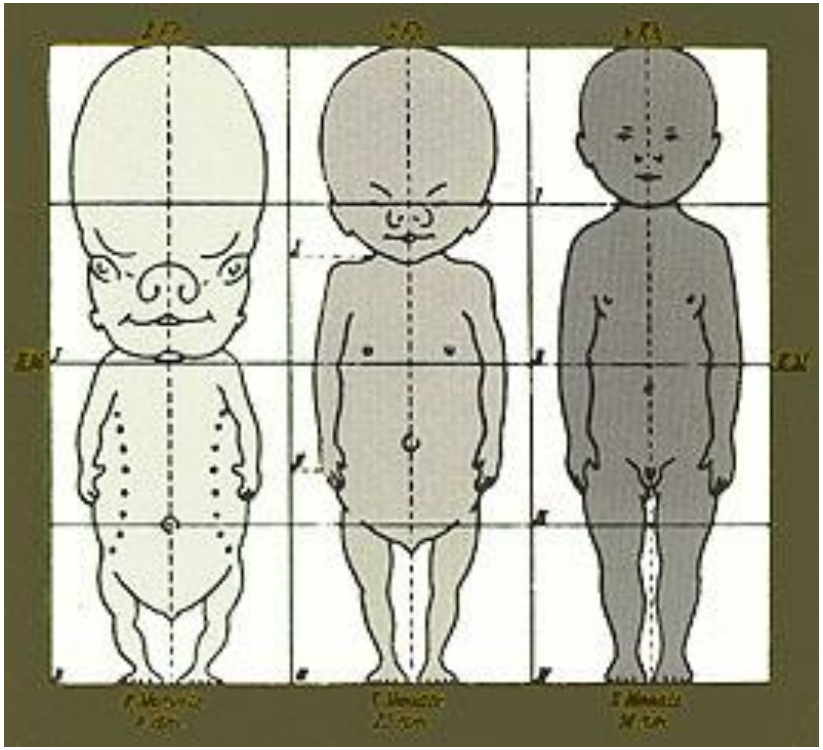
Growth as a challenge

Biological organisms need to be functional at any development and growth stage!

Exterior skeleton

molting insect: shedding of exoskeleton makes insect vulnerable

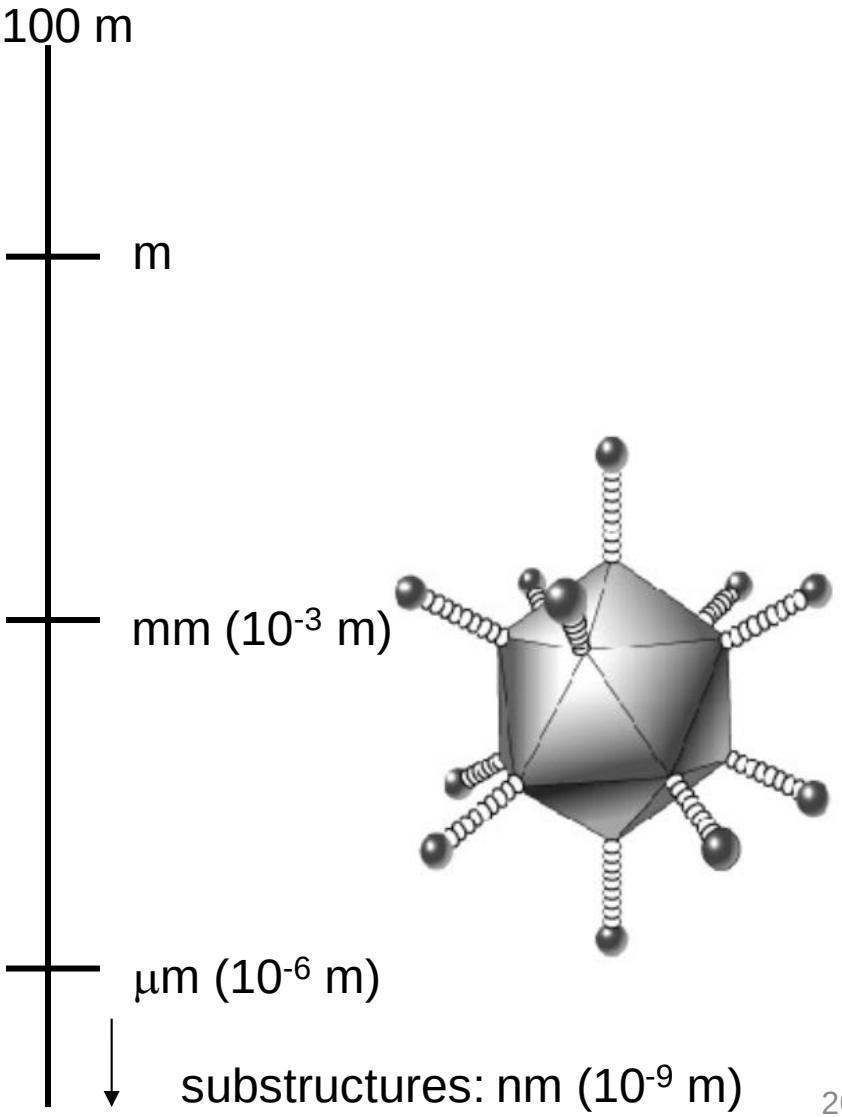
Interior skeleton



humans: skeleton can grow

1. Introduction

Structures on many length scales



1. Introduction

Challenge for materials scientists

Material or structure?

1. Introduction

Summary

Biomaterials are....

- made from metabolically cheap substances
- light weight (efficient design)
- able to respond to changes of conditions by adaptive growth
- mechanically optimized to specific loading pattern
- structured on many different length scales (hierarchical architecture)
- designed to grow while keeping full functionality

This lecture ....

Scope:

- elements of biomaterials
- design concepts & consequences
- mechanical properties
- adaptatation strategies
- learning from biology
- selected examples

Limitations:

- not each and every biomaterial is covered
- only „structural biomaterials“

2. Elements of biological materials

Components of biological materials

organic compounds:
carbon compounds, containing carbon-hydrogen bonds

organic

Proteins
chains of amino acids

major organic component in animals
(skin, tendon, bone, cartilage...)

Polysaccharides
chains of sugars

major organic component in plants
(cellulose)

inorganic: water, salts -> Biomineralization (chapter 7)

inorganic compounds:
non-carbon compounds excepting elemental carbon (graphite, diamond) or carbon oxides

2. Elements of biological materials

2.1 Proteins

Tasks:

- enzymatic catalysis
- transport and storage (e.g. oxygen in blood)
- coordination of motion
- mechanical support: collagen
- immune defense: antibodies
- creation and transmission of nervous impulses
- control of growth and differentiation of cells

Shape:

structural proteins mostly ***fibrous*** (especially in animals), some also as fillers

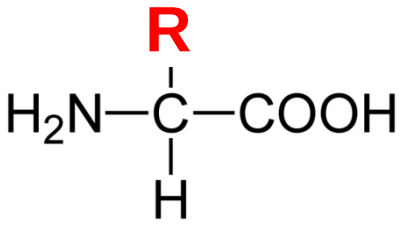
2. Elements of biological materials

2.1.1. Basic facts and structure of proteins

Structure of a protein

Proteins are chains of amino acids.

Naturally occuring: about 20 different amino acids.



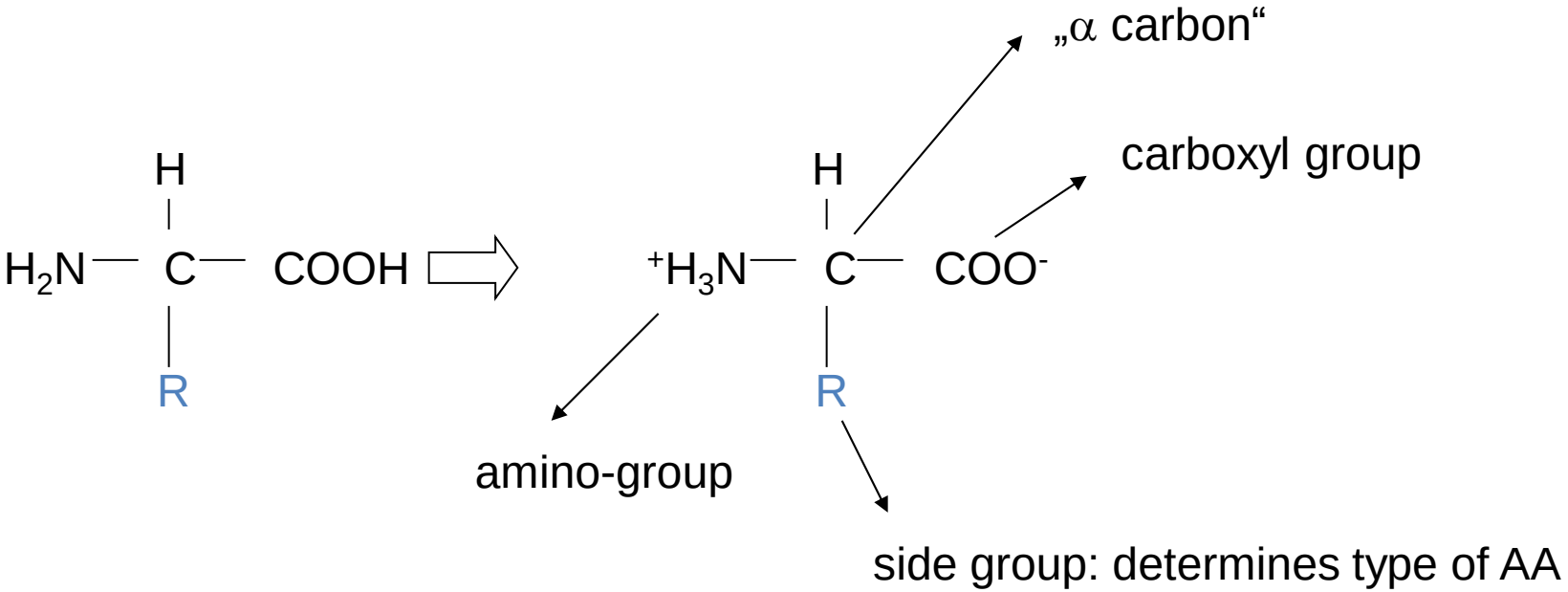
Chemical and physical properties determined by side group R

- Polar (hydrophilic)
- Non-polar (hydrophobic, water repellent)
- Positively charged (base)
- Negatively charged (acid)

2. Elements of biological materials

Amino acids

Basic structure

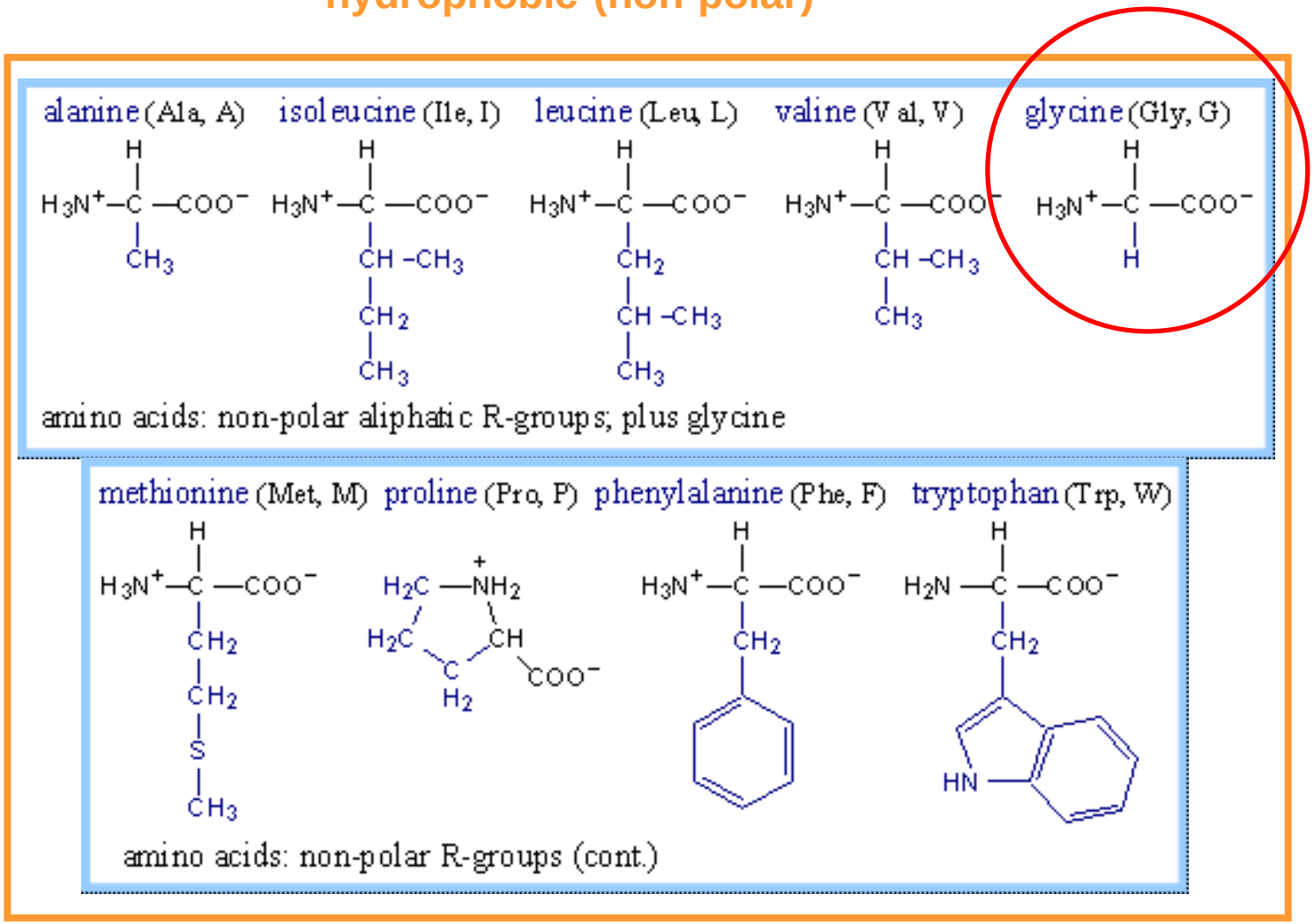


zwitter-inonic form of amino acid (AA),
at neutral pH (pH=7)

2. Elements of biological materials

Types of amino acids

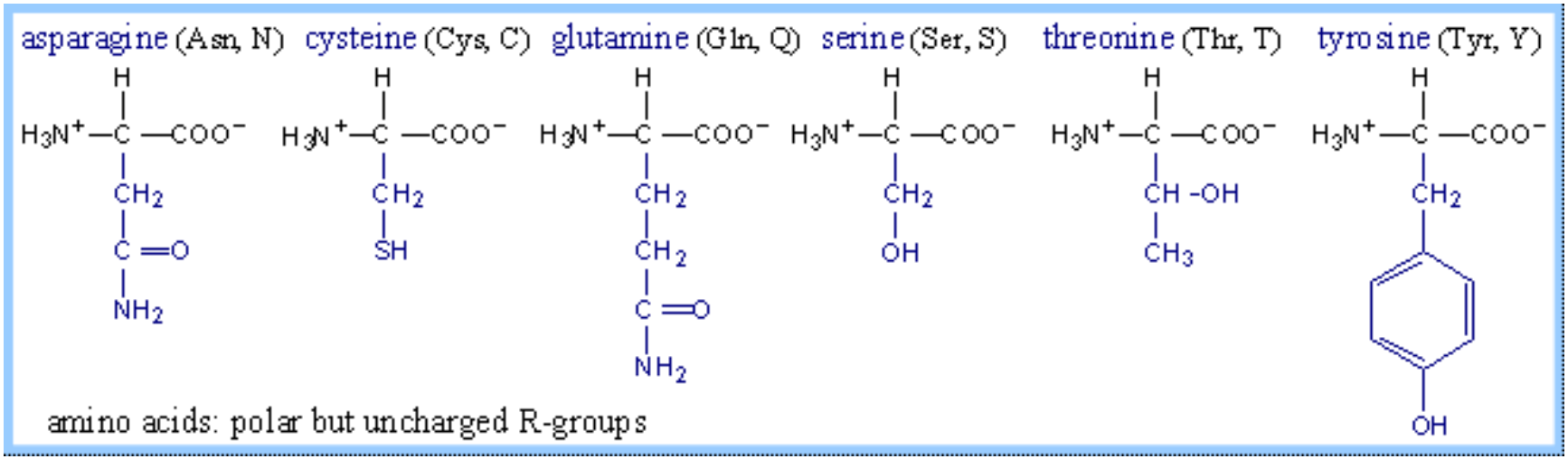
hydrophobic (non-polar)



2. Elements of biological materials

Types of amino acids

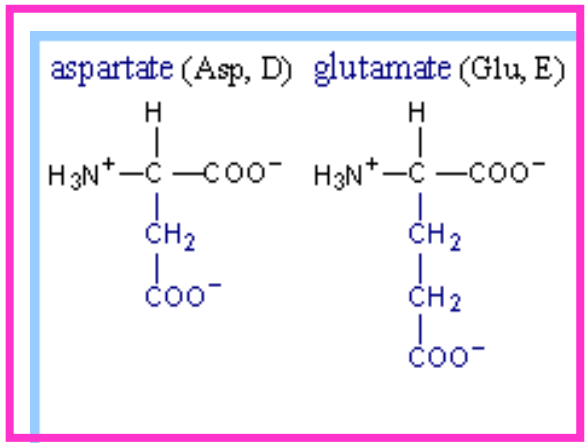
hydrophilic (polar)



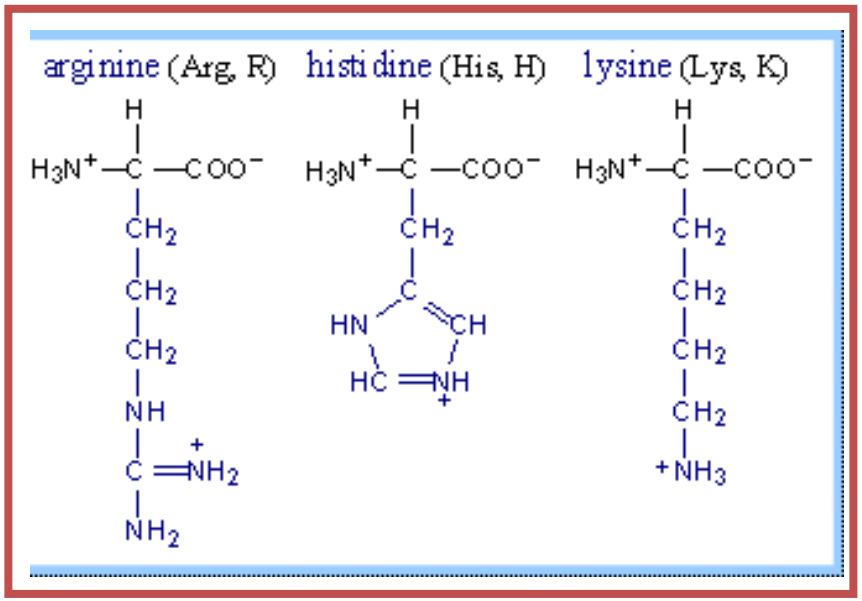
2. Elements of biological materials

Types of amino acids

Charged:

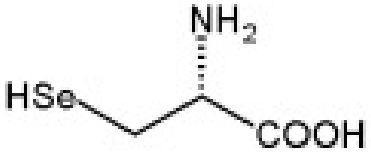


acid

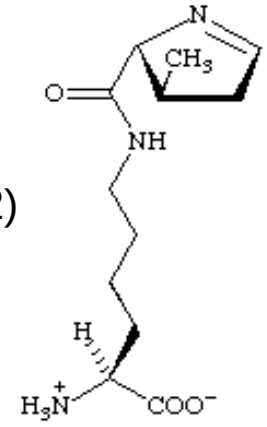


base

+ selenocysteine (1986)



+ pyrrolysine (2002)



Source: http://www.rpi.edu/dept/bcbp/molbiochem/MBWeb/mb1/part2/protein.htm

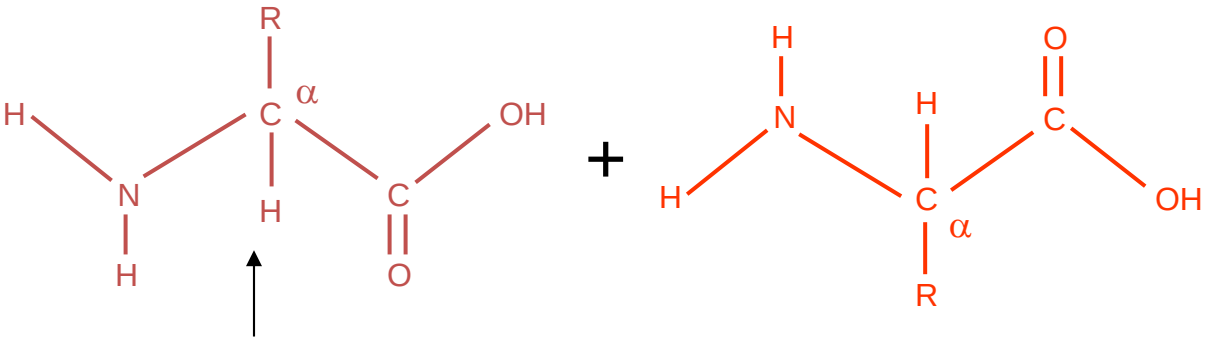
2. Elements of biological materials

Primary structure of a protein:

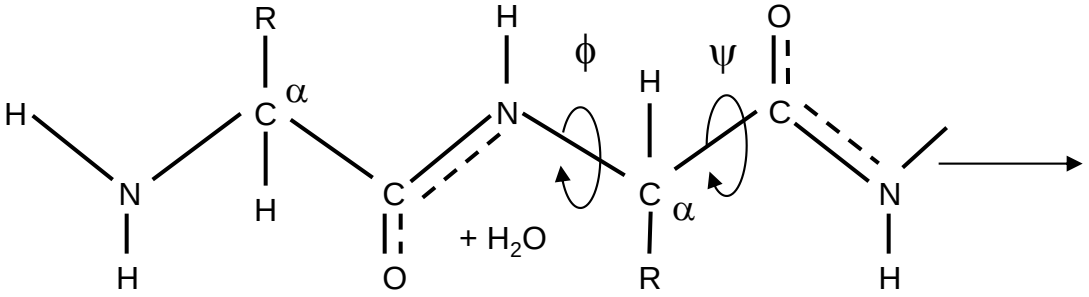
Sequence of amino acids is called primary structure!

Protein chain forms via condensation reaction:

2 neighboring amino acids join by forming a peptide bonde (amide link)



basic structure of amino acid

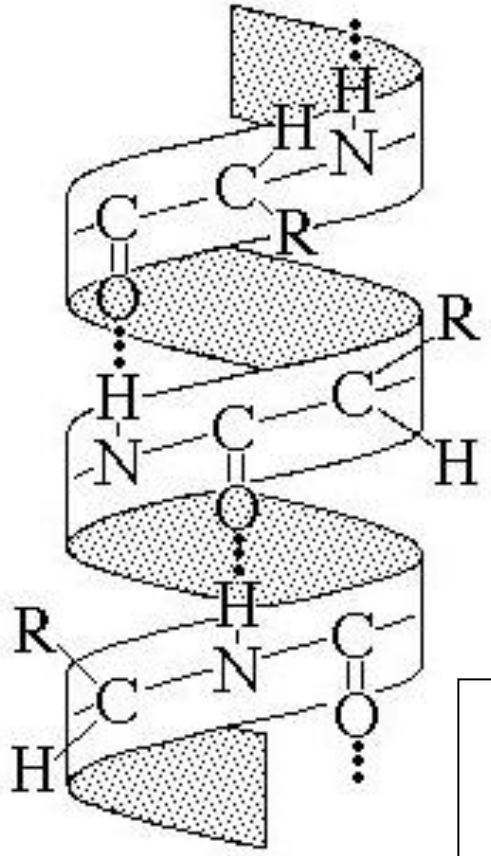


primary structure: protein chain

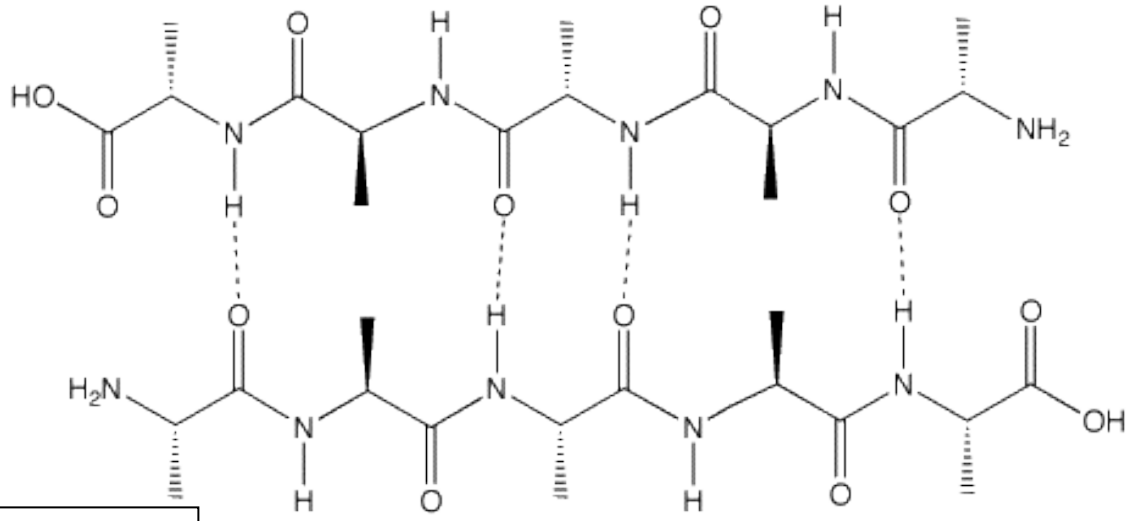
2. Elements of biological materials

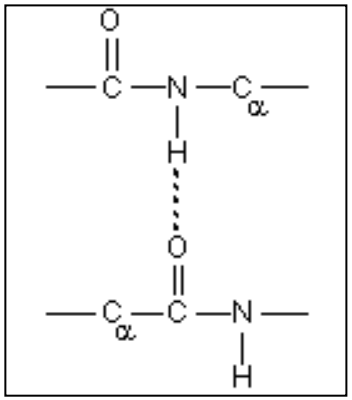
Secondary structure

1. Alpha –Helix



2. Beta-strand (single AA chain)/ **Beta-sheet**



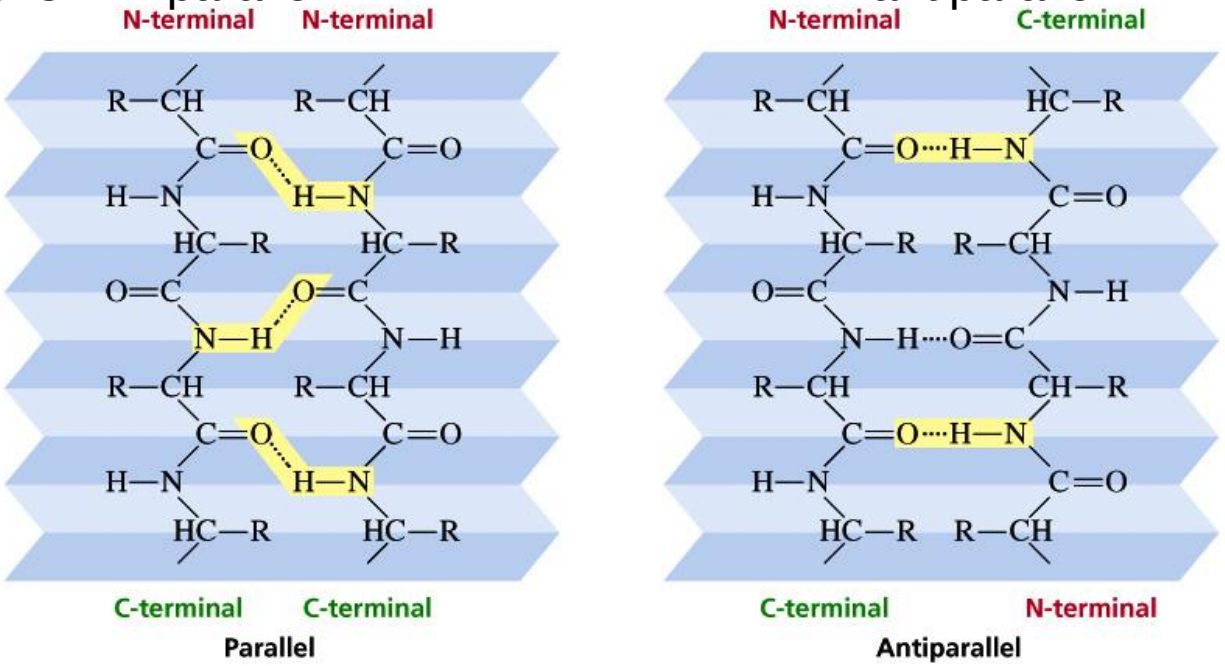


Stabilized by hydrogen bonds!

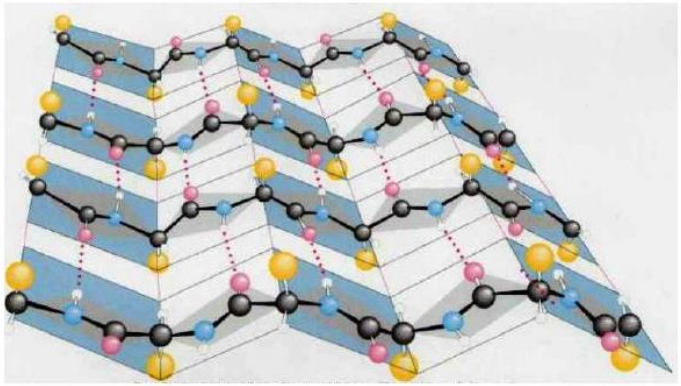
2. Elements of biological materials

Beta sheet:

2 conformations: parallel antiparallel



View in 3D:

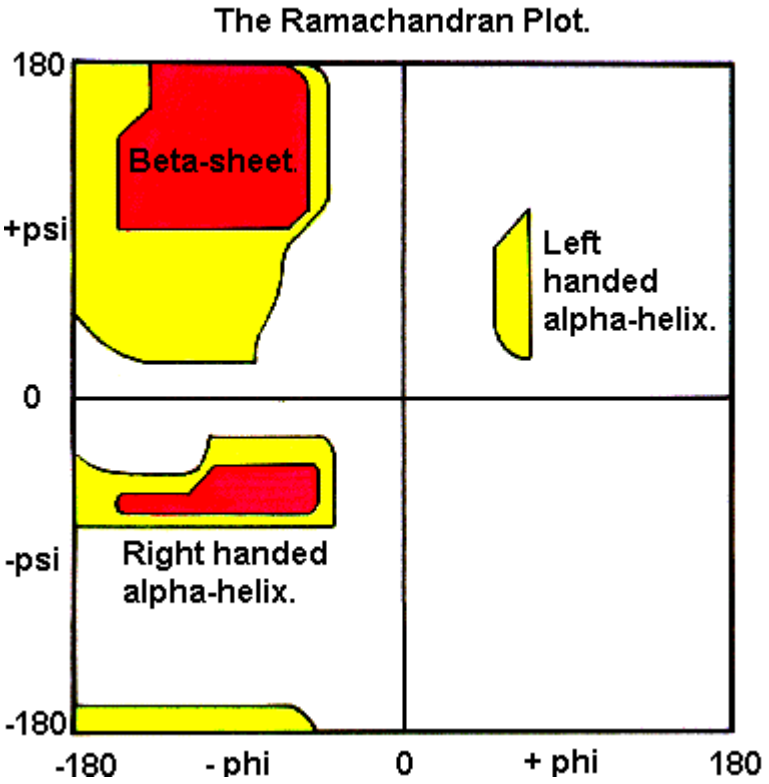


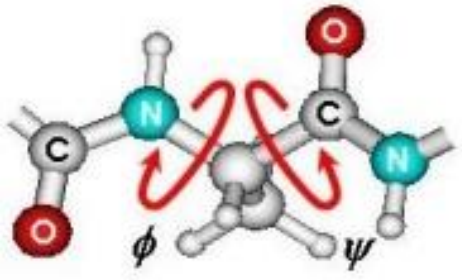
2. Elements of biological materials

Protein conformation, Ramachandran plot

Whether alpha-helix or beta-sheet is preferred, depends on possible rotation angles ϕ and ψ of protein chain around alpha carbon.

Ramachandran plot describes possible secondary structure as function of ϕ and ψ.





2. Elements of biological materials

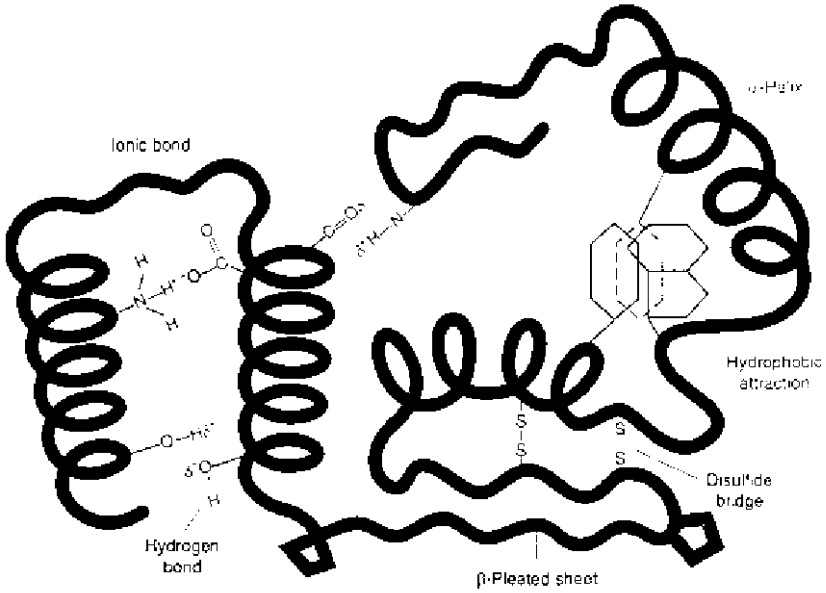
Amino acids and secondary structure

Depending on the chemical and structural nature of the different amino acids, they have a tendency to be involved in helix formation or beta sheets.

helix breaker	helix indifferent	helix former
Glycine	Lysine	Valine
Serine	Tyrosine	Glutamine
Proline	Threonine	Isoleucine
Asparagine	Arginine	Histidine
Aspartic acid	Cysteine	Alanine
	Phenylalanine	Tryptophan
		Leucine
		Methionine
		Glutamic acid

2. Elements of biological materials

Tertiary structure: folding of a protein



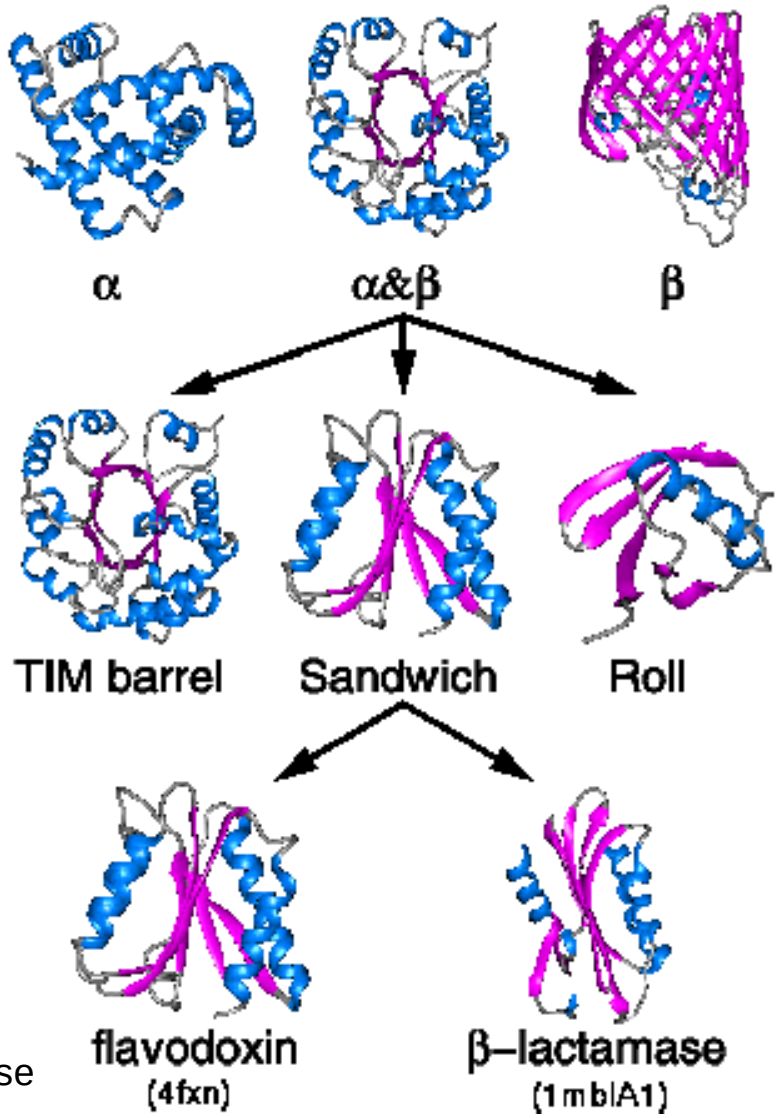
Determined by chemical nature of amino acids (acidic, basic, polar, non-polar)

In water: hydrophilic groups mostly on the outside of molecule (or bound by H-bonds inside), hydrophobic groups inside, in lipid: other way round (often leads to globular proteins)

Most proteins have stricly defined tertiary structure, closely connected to their functionality.

2. Elements of biological materials

Examples of tertiary structures



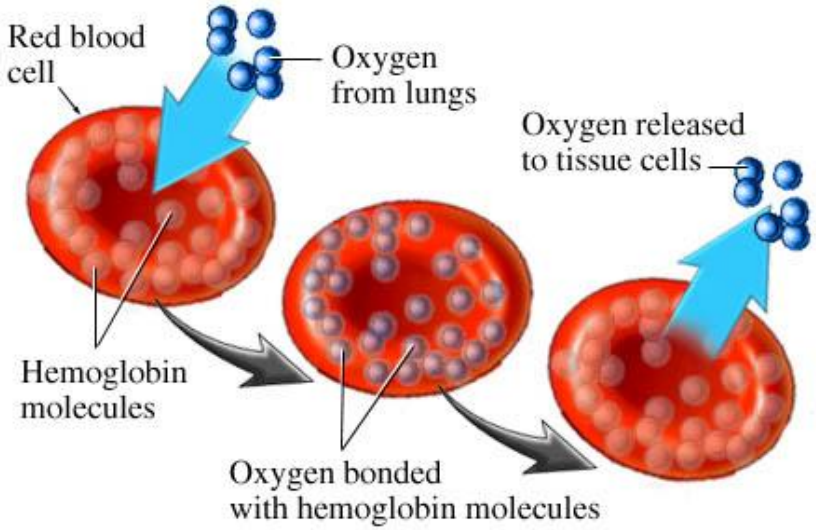
TIM: Triosephosphate isomerase

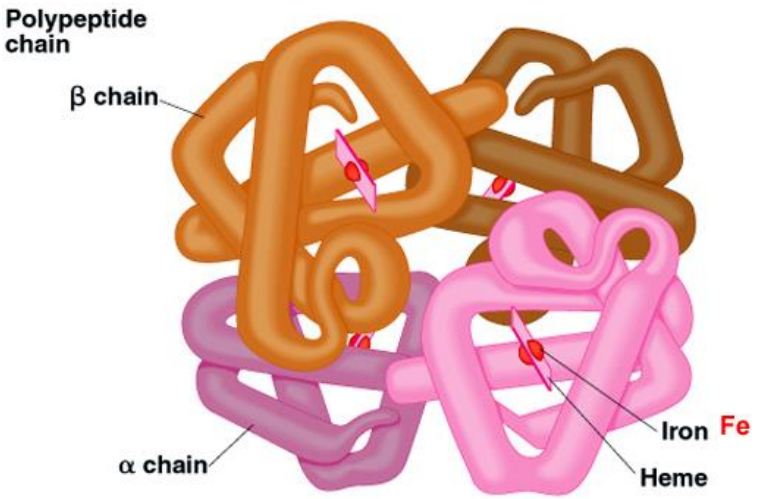
2. Elements of biological materials

Quaternary structure

Example: hemoglobin in red blood cells

red blood cells





(b) Hemoglobin

hemoglobin molecule:
4 subunits

2. Elements of biological materials

Summary, protein basics

Primary structure: proteins consist of amino acids.

Secondary structure: proteins form helices or sheets

Tertiary structure: folding of protein

Quaternery structure: assembly or large functional units: example: hemoglobin

2. Elements of biological materials

Types of protein

structural

fibrous:

- keratin (hair, wool, hoof,...)
- silk (silkworm silk, spider silk)
- collagen (skin, tendon, bone,...)

fillers (protein rubbers)

- elastin
- abductin
- resilin

enzymatic

antibodies

storage

etc. etc...

2. Elements of biological materials

Examples of structural proteins

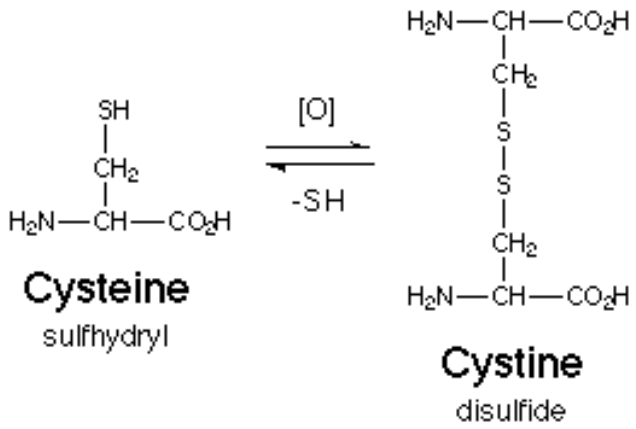
- 2.1.2 Keratin
- 2.1.3 Silk
- 2.1.4 Collagen
- 2.1.5 Filler proteins

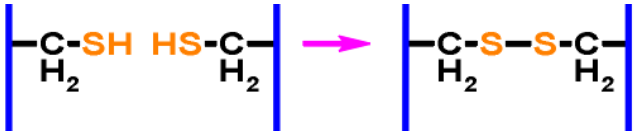
2. Elements of biological materials

2.1.2 Keratin

Structural, fibrous protein found in horn, hair, hoof, feathers etc.

Important component: amino acid cysteine





Forms disulphide bonds with cysteine from neighboring protein chain -> covalent (strong bonds)

Did you know that
the nasty smell when horn, hair, hoof, feather etc. is burned comes from sulphur

2. Elements of biological materials

Amino acid composition of some keratins

Amino acid	High sulphur proteins			Low sulphur proteins		
	Wool	Horn	Hoof	Wool	Horn	Hoof
Lys	0.6	1.0	1.0	4.1	4.1	5.0
His	0.7	1.0	0.9	0.6	0.8	0.8
Arg	6.2	5.4	6.0	7.9	7.8	7.1
Asp	2.3	4.7	4.3	9.6	8.9	10.1
Thr	10.2	9.6	10.2	4.8	4.9	4.4
Ser	13.2	11.2	11.8	8.1	8.4	7.8
Glu	7.9	6.1	6.9	16.9	15.8	17.7
Pro	12.6	12.4	13.0	3.3	3.6	2.4
Gly	6.2	9.0	7.2	5.2	6.9	6.3
Ala	2.9	3.2	3.2	7.7	7.4	7.2
Cys½	22.1	16.3	16.9	6.0	4.7	3.7
Val	5.3	5.6	5.8	6.4	6.2	5.9
Met	0	0	0	0.6	0.7	0.7
Ile	2.6	3.3	3.2	3.8	3.8	3.9
Leu	3.4	5.3	4.9	10.2	10.1	11.1
Tyr	2.1	3.3	2.3	2.7	3.3	3.2
Phe	1.6	2.6	2.4	2.0	2.5	2.0
Helix breaker	34.4	37.3	36.3	24.3	27.8	26.6
Helix former	22.8	24.5	24.9	46.1	44.8	47.3
Helix indifferent	42.7	37.9	38.9	27.5	27.3	25.4
Percentage sulphur (total)	3.75	2.13	2.15			

From Marshall & Gillespie (1977)

From Vincent 1990.

Horn contains a great number of high sulphur proteins: mechanically most stable (heavily cross-linked)

2. Elements of biological materials

Hair keratin (α-keratin)

Fibrous keratin, secondary structure: helix

Hierarchical structure

- 2 alpha-helices yield superhelix (protofibril)
- several protofibrils yield microfibril

Keratin fibers embedded in non-fibrous matrix with high amounts of Cys, Ser and Pro

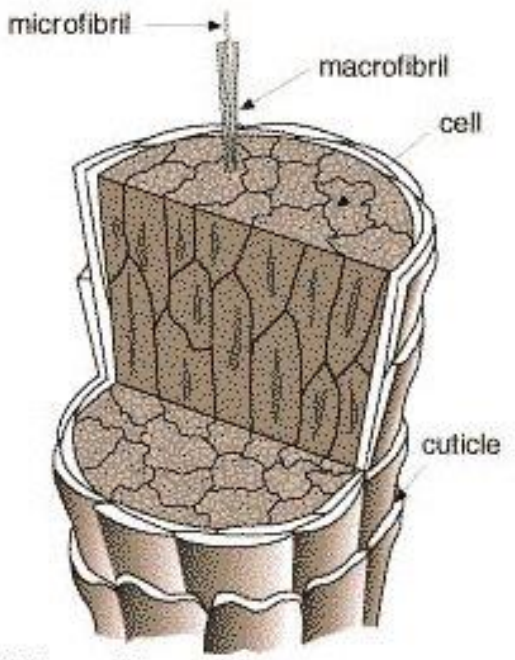


Figure 10a

The organisation of a complete hair.

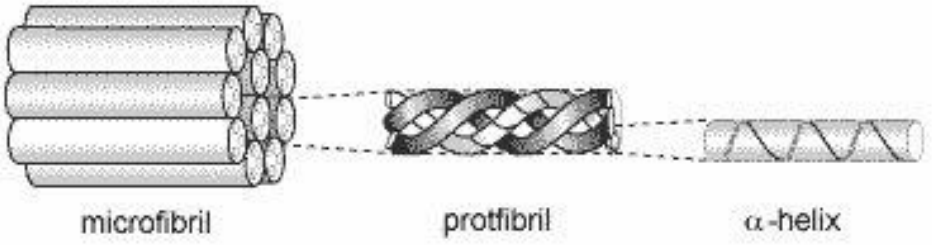


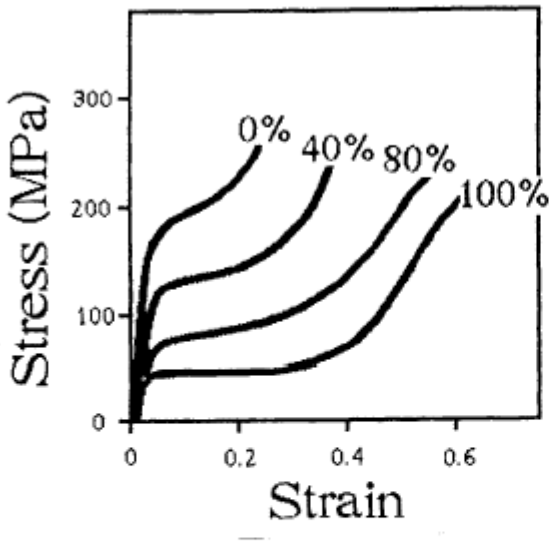
Figure 10b

Hair α-keratin

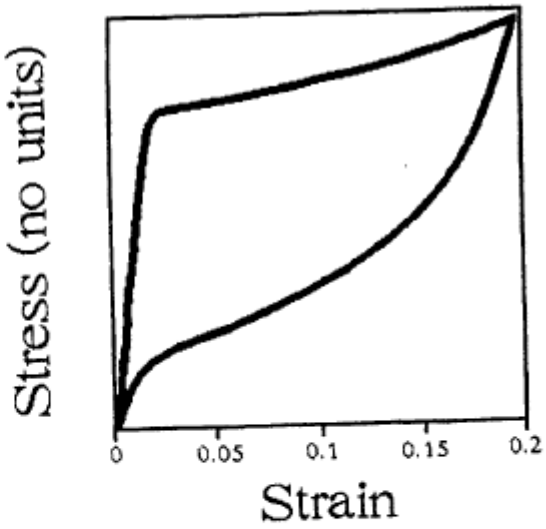
2. Elements of biological materials

Mechanical properties of hair keratin

- Hydration dependent (softening by water)
- Highly viscoelastic



Mechanical properties of α-keratin as typified by wool at different relative humidities (Hearle et al. 1971).
From Vincent 1990.



Hysteresis of α-keratin in hair.
From Vincent 1990.

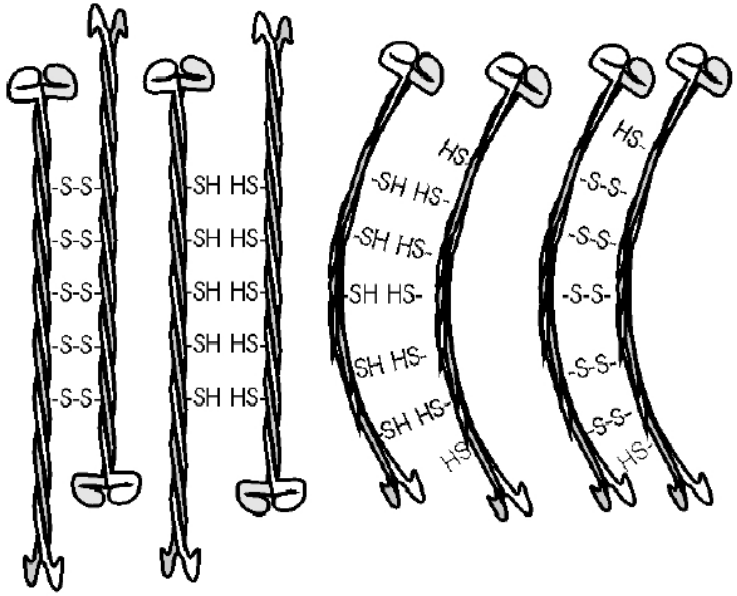
2. Elements of biological materials

Structural and chemical background of hairstyling

Hair setting: soaking with water breaks hydrogen bonds, re-set during drying. Process more effective by heating (hair dryer).

Disulfphide bonds remain unaffected → hair adopts its natural shape when washed again.

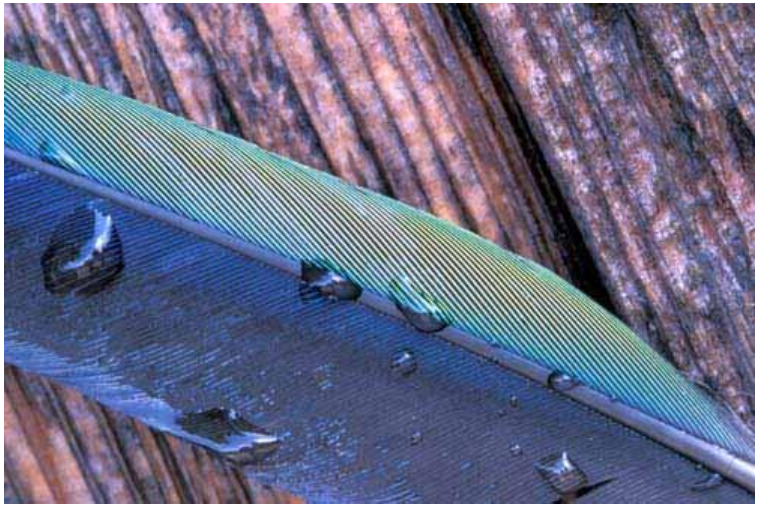
Permanent waving/ straightening: Disulphide –S-S- bonds are chemically reduced to –SH, molded into shape, re-oxidized.

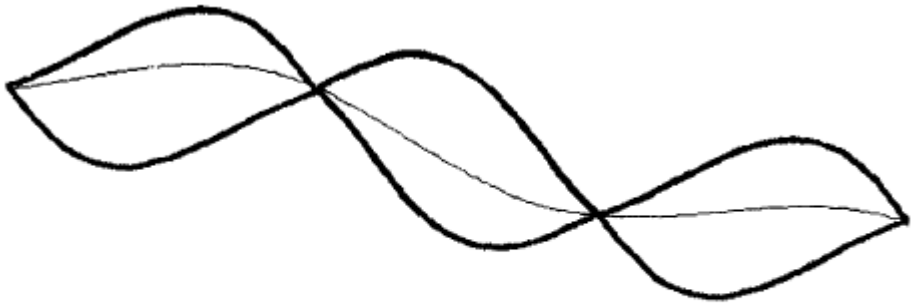


2. Elements of biological materials

Feather keratin

Fribrous protein, more Gly, Ser and Pro than in alpha keratin.





Twisted beta structure of feather keratin.

Table 2.3 Amino acid composition of feather keratin

Arg	4.1	Gly	16.4
Cys	7.2	Ala	7.4
Asp	5.1	Val	8.7
Thr	4.8	Leu	2.4
Ser	10.8	Ileu	7.7
Glu	7.8	Tyr	3.0
Pro	11.1	Phe	3.7

From O'Donnell & Inglis (1974)

2. Elements of biological materials

Mechanical properties of feather keratin

- Twice as stiff as hair
- very elastic (small hysteresis), no abrupt modulus changes up to deflection typically occuring during flight

Structural properties

- at either end: non-crystalline sections rich in cystine
- at the center: large crystalline region with many **hydrophobic** residues

stability of interactions is increased in aqueous environment

2. Elements of biological materials

2.1.3 Silk

Fibrous structural protein, based on beta sheets, not occuring in human body

Types of silk:

- **Silkworm silk** (used for production of clothing etc.): soft, pleasant texture
- **Spider silk:** stiff and tough, complicated structure

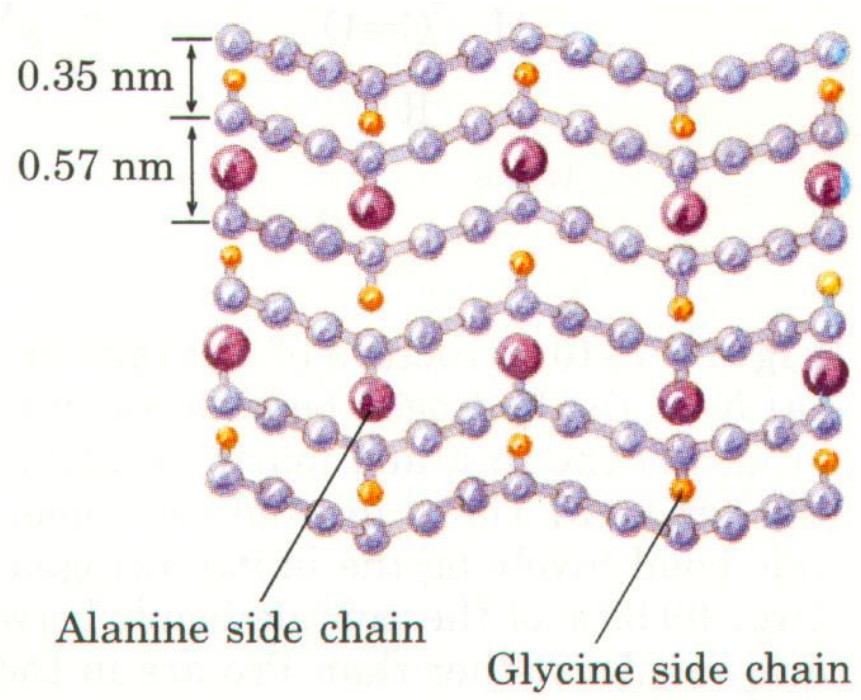
2. Elements of biological materials

Silkworm silk

silkworm: Bombyx mori (common silk-worm)

Structure of silkworm silk:

Beta sheet, regular arrangement of Ala and Gly



2. Elements of biological materials

Amino acid composition of silk worm silk

Table 2.4 Amino acid composition (%) of *Bombyx* silk

Gly	44.5	Lys	0.3
Ala	29.3	Arg	0.5
Val	2.2	His	0.2
Leu	0.5	Tyr	5.2
Ile	0.7	Phe	0.6
Ser	12.1	Pro	0.3
Thr	0.9	Try	0.2
Asp	0.3	Met	0.1
Glu	1.0		

From Lucas & Rudall (1968)

Helix breakers or helix formers?

Forces keeping silk worm silk together:

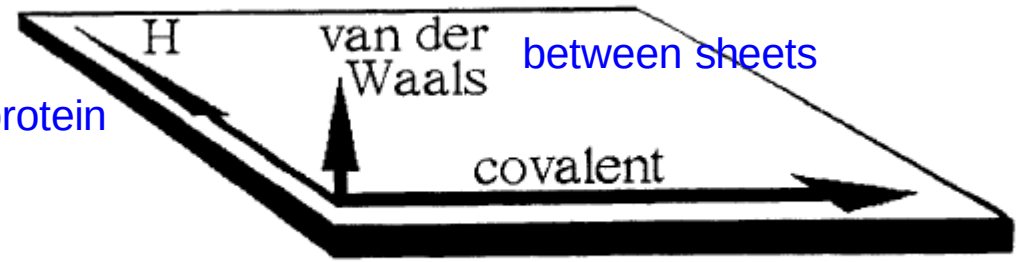


Figure 2.16 The major forces stabilizing silk β-sheet structure.

Consequence: weak van der Waals bonding between sheets causes pliability (softness of fiber)

2. Elements of biological materials

Spider silk

Very strong and light weight fiber.

„Stronger than steel“ (at least weight for weight)

Possibly applications, myths and phantasies:

Spiderman

Bullet proof vests

Rope for space elevator

2. Elements of biological materials

Types of spider silk

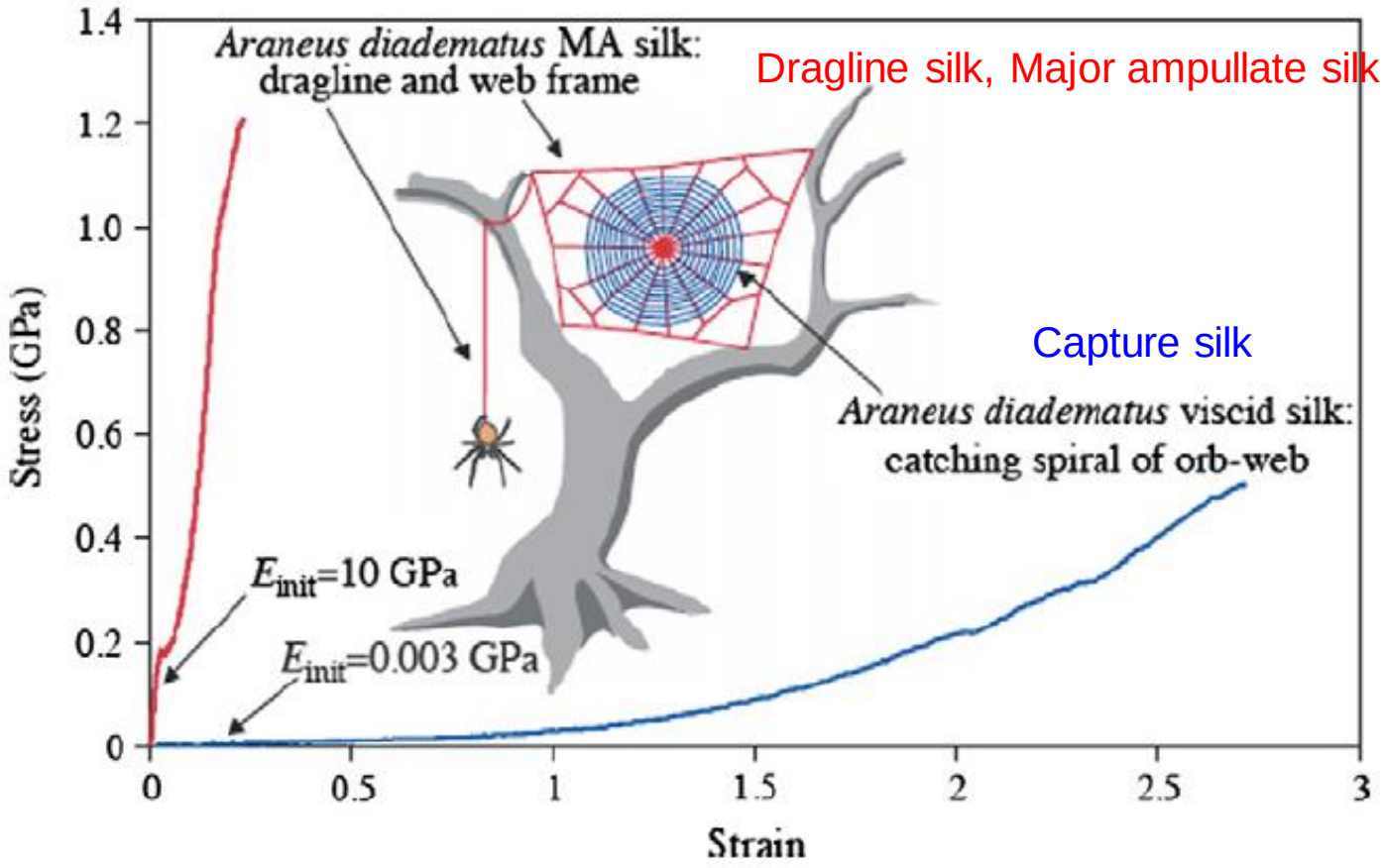


Fig. 11. Stress–strain curves for major ampullate (MA) gland (red) and viscid silk (blue) from the spider *Araneus diadematus*. E_{init} = initial stiffness. Taken from [102].

Gosline JM, et al. J Exp Biol 1999;202:3295–303.

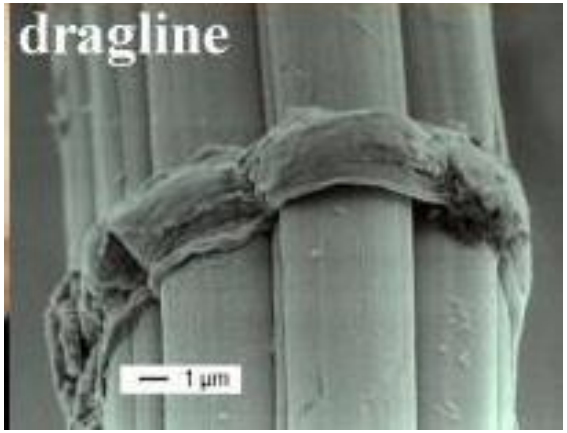
2. Elements of biological materials

Dragline silk

Major ampullate silk (MAS): frame, supporting radii, abseiling thread

High strength, thicker fibers, spun at 1-10 cm/s (web building or „abseiling“), failure strain 20 %

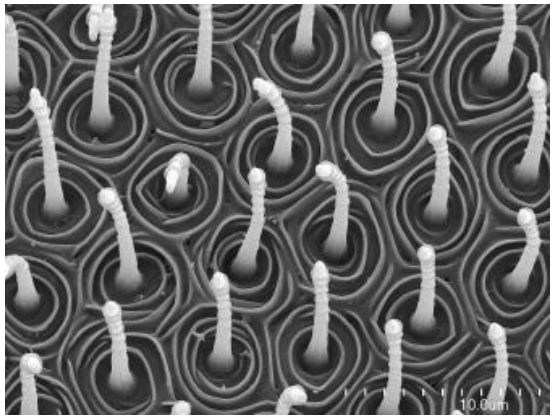
Mechanical properties vary with production process, e.g. forced siliking yields inferior properties.



2. Elements of biological materials

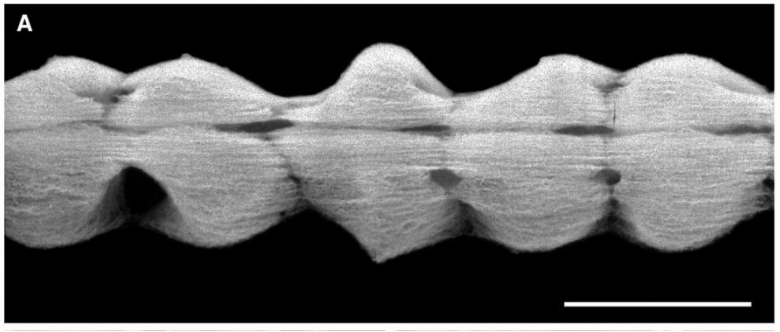
Capture silk

Cribellate silk: capture silk from spiders having a cribellum



Cribellum: plate with spigots

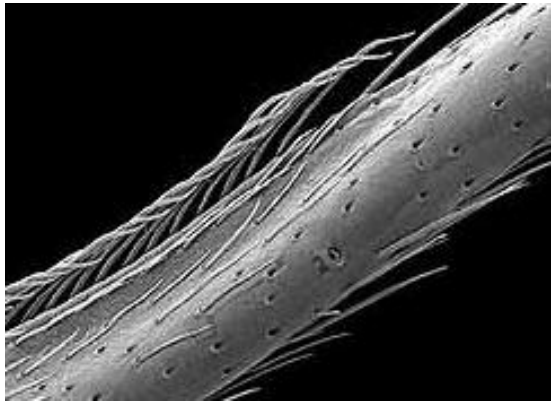
Cribellate capture silk: nanofibers



Cribellar thread of *Hyptiotes cavatus* (scale bar, 150 μm)

Hawthorn, A. C. et al. J Exp Biol 2003;206:3905-3911

Stickiness without glue!

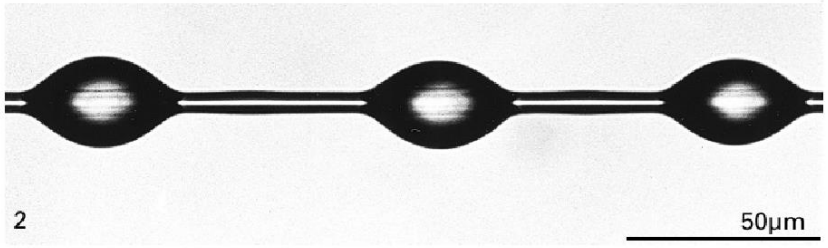


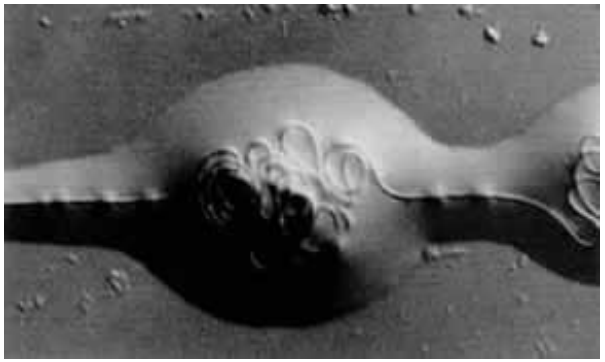
Threads combed with Calamistrum

2. Elements of biological materials

Ecribellate capture silk (viscid silk)

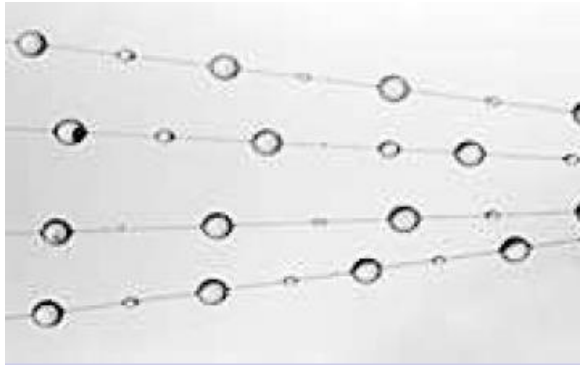
Capture silk from spiders not having a cribellum





Light micrograph of the adhesive capture thread of *Argiope trifasciata,* covered with sticky glue:

Glue is highly hygroscopic, large surface energy, minimizes contact with air, forms round droplets



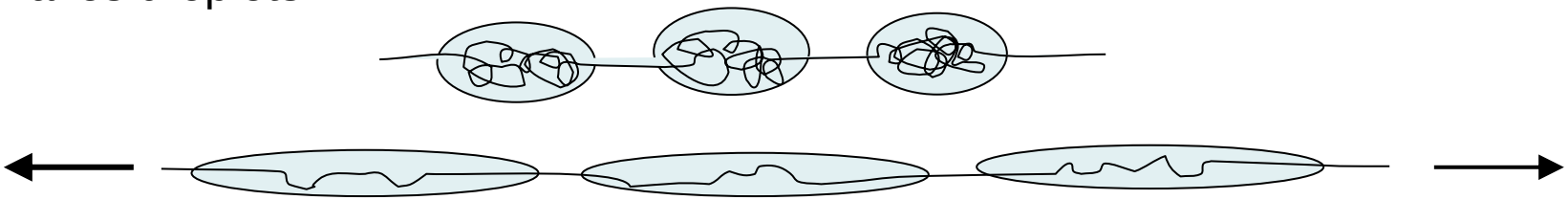
Maximum strain, dry 200%
Maximum strain with glue 500%

2. Elements of biological materials

Capture thread with sticky glue

„Windlass“-mechanism proposed by Vollrath *et al.* for ecribellate orb web spiders

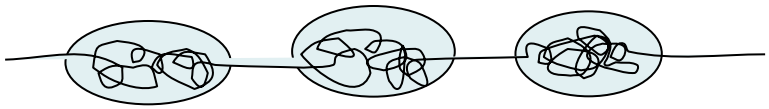
1. Relaxed state:
glue makes droplets



2. Droplets get extended.
Energetically unfavorable,
since large contact area of
glue with air

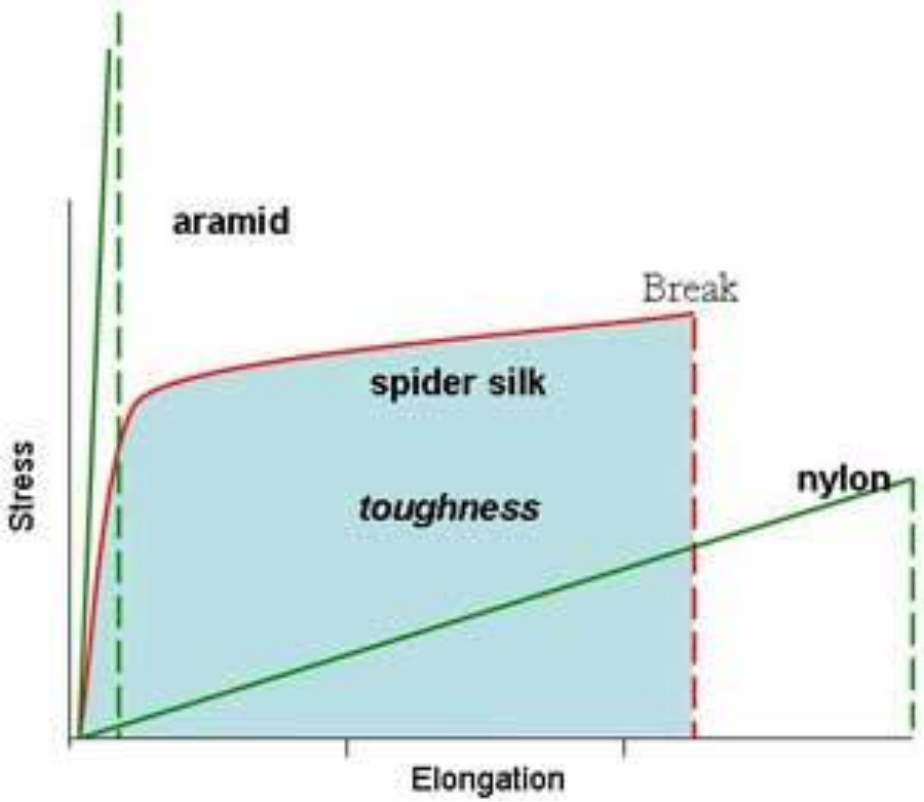
Release:

3. Glue droplets snap
back into round shape,
take fiber coil with them



2. Elements of biological materials

Mechanical properties of spider silk



- **Strength versus density**: 5 times as strong as steel (high strenth steel: 1,5 GPa, spider silk 1.1 GPa, density of steel about 8 kg/dm^3, density of silk: 1-1.5 kg/dm^3)
- **Very high toughness**

2. Elements of biological materials

Mechanical Properties of spider silk in numbers

Material	Tensile Strength	Extensibility	Fracture Energy
Bone	150 MPa	2 %	1,500 J/kg
Mild Steel	350 MPa	40 %	13,000 J/kg
High-Strength Steel	1500 MPa	0.8 %	800 J/kg
Kevlar	3600 MPa	2.7 %	35,000 J/kg
Spider Silk I (MAS)	1100 MPa	30 %	150,000 J/kg
Spider Silk II (viscid silk)	500 MPa	800 %	140,000 J/kg

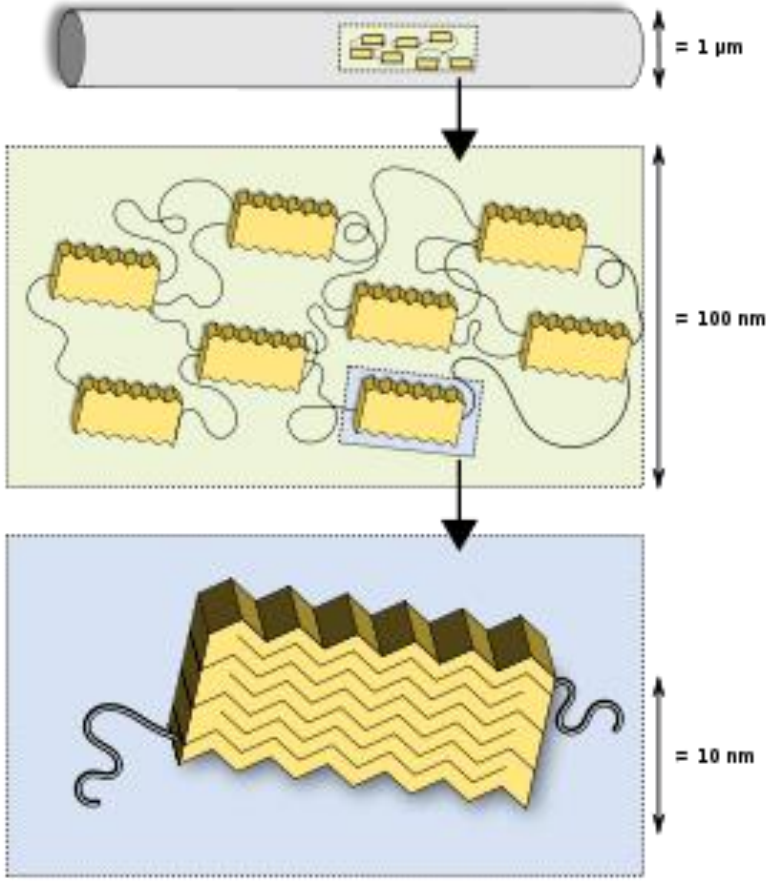
Courtesy Martin Baeker, TU Braunschweig

2. Elements of biological materials

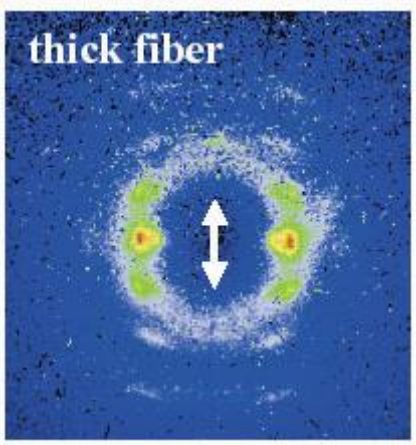
Composition of spider silk

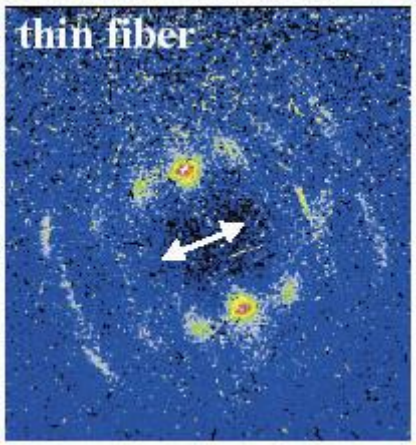
Spider silk consists of protein with high amount of Glycin und Alanin (similar to silkworm silk)

Secondary structure: beta sheet, fibers are partly crystalline



X-ray diffraction patterns of spider silk

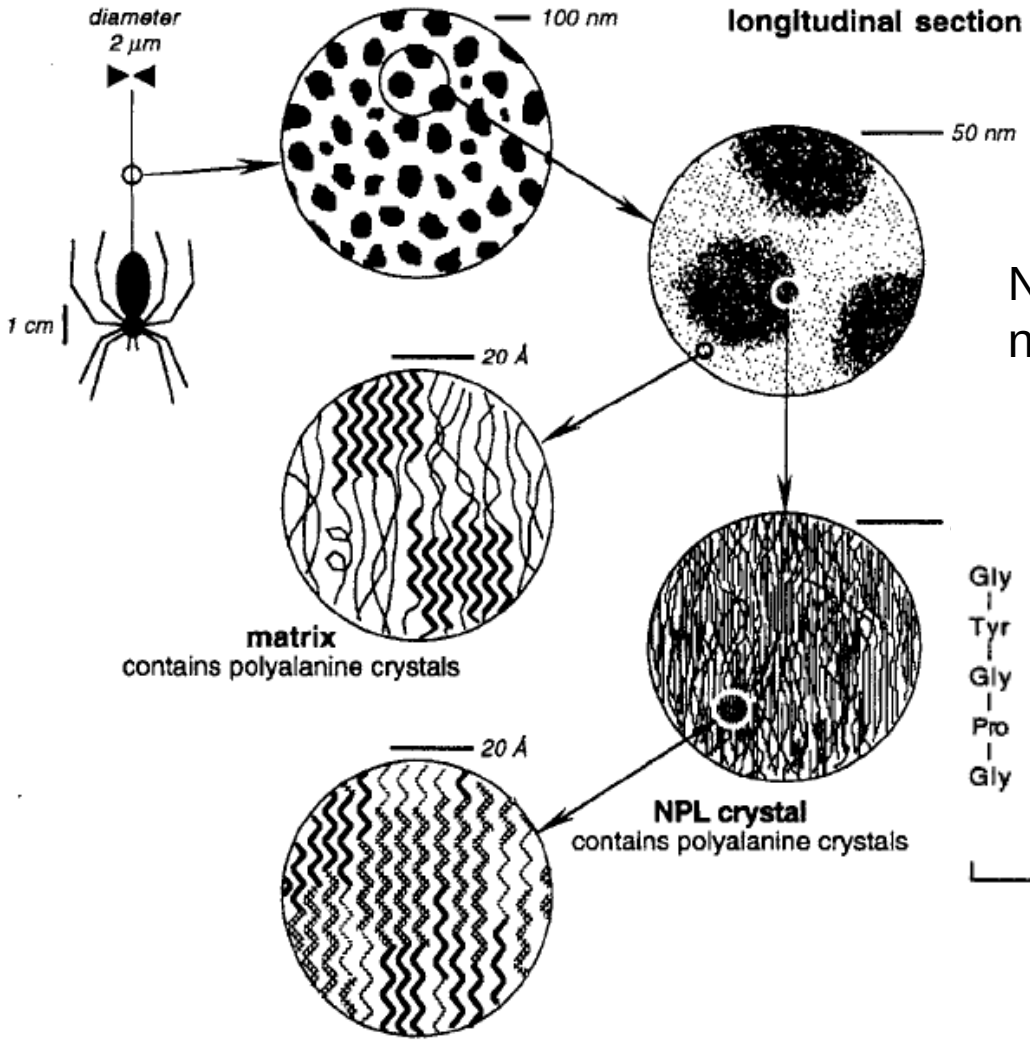




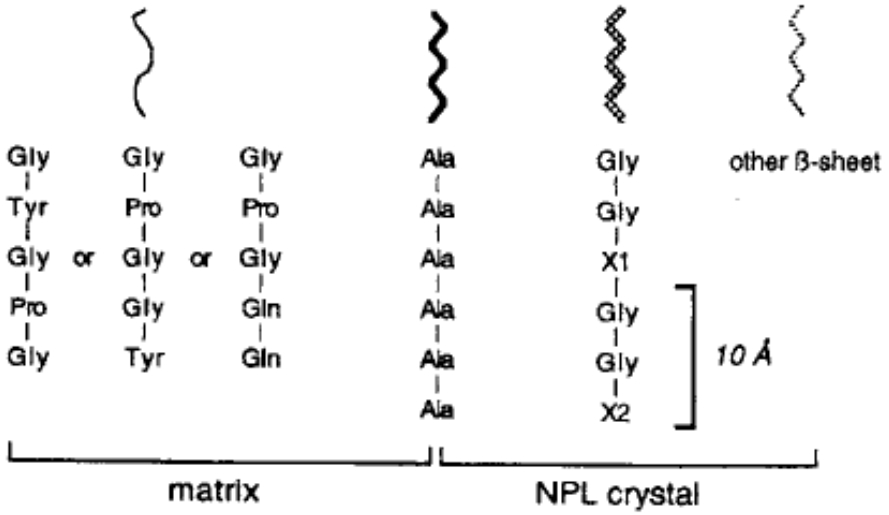
2. Elements of biological materials

Structure of spider dragline silk

Complex nanocomposite structure, crystalline particles in non-crystalline matrix



NPL crystal:
non-periodic lattice crystal

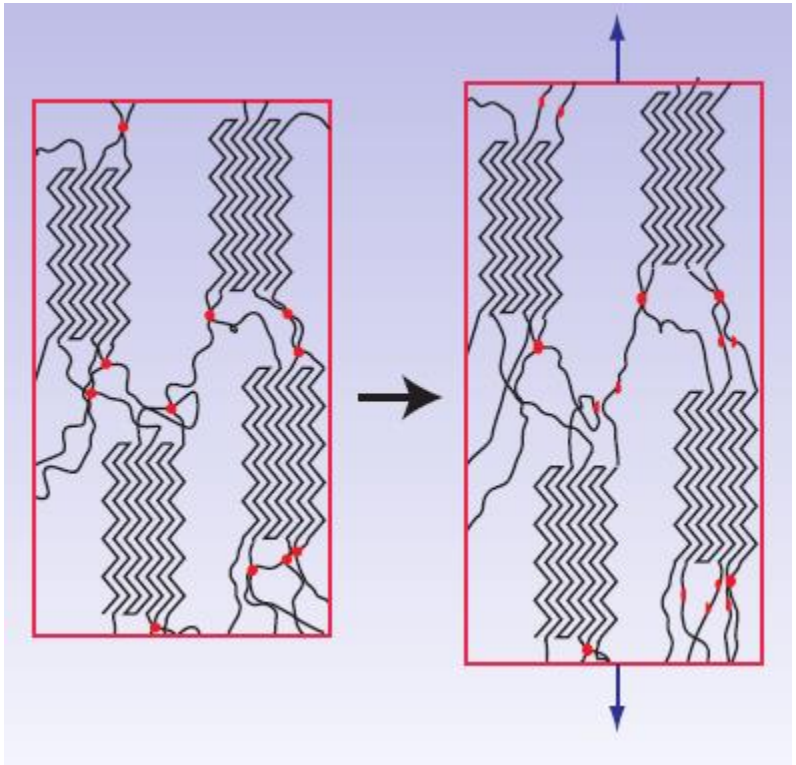


2. Elements of biological materials

Mechanical behavior of spider silk

Particle reinforced composite: protein crystals in protein matrix

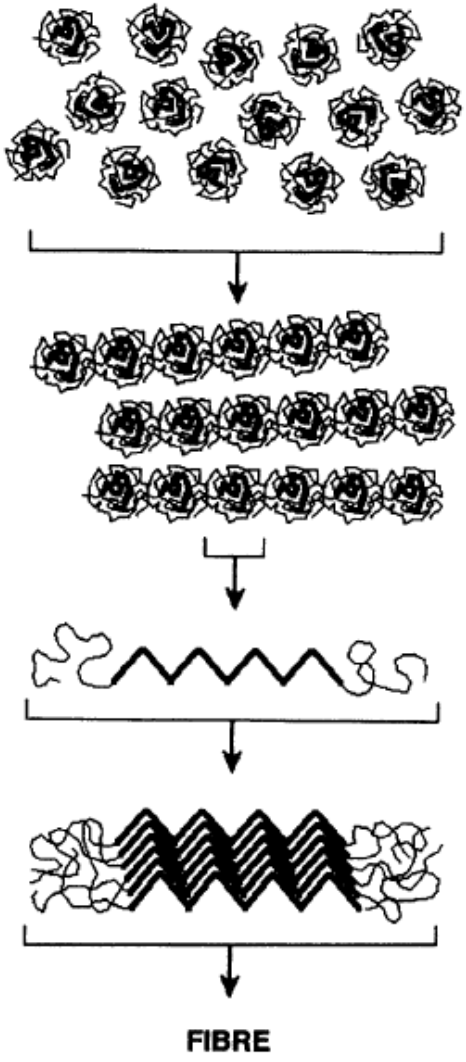
Deformation: matrix is deformed plastically, rigid particles carry load



Courtesy Martin Baeker, TU Braunschweig

2. Elements of biological materials

Spinning of spider silk



Silk stored in gland
Globular molecules (water soluble)
Optically isotropic
Less shear sensitive

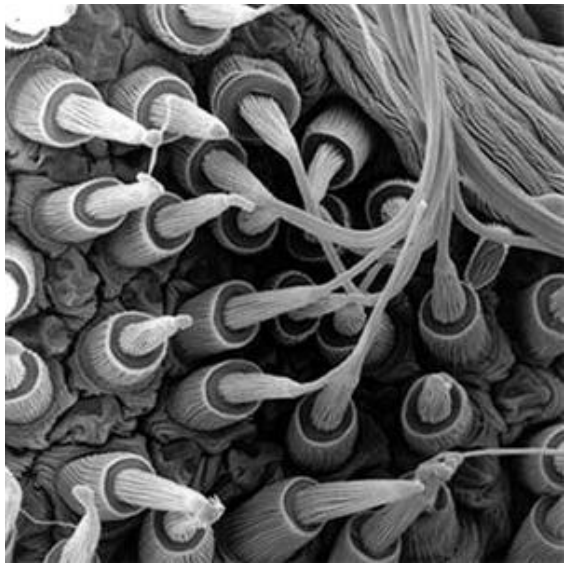
Silk in duct leading to spinneret
Anisotropic aggregates of globular molecules (water soluble)
Optically anisotropic (birefringence)
More shear sensitive, liquid crystalline

Silk at spinneret
Shear-induced transition to crystalline beta sheet (insoluble in water)
Optically anisotropic (orientation birefringence)

From Elices, Structural Biological Materials (2000), Pergamon

2. Elements of biological materials

Silk production



Spinnerets

Seven types of silk produced by seven silk glands.
Single spider has at least three glands if it is male (dragline, attachment and swathing silk) or four if it is female.
The additional one is for egg sac silk.

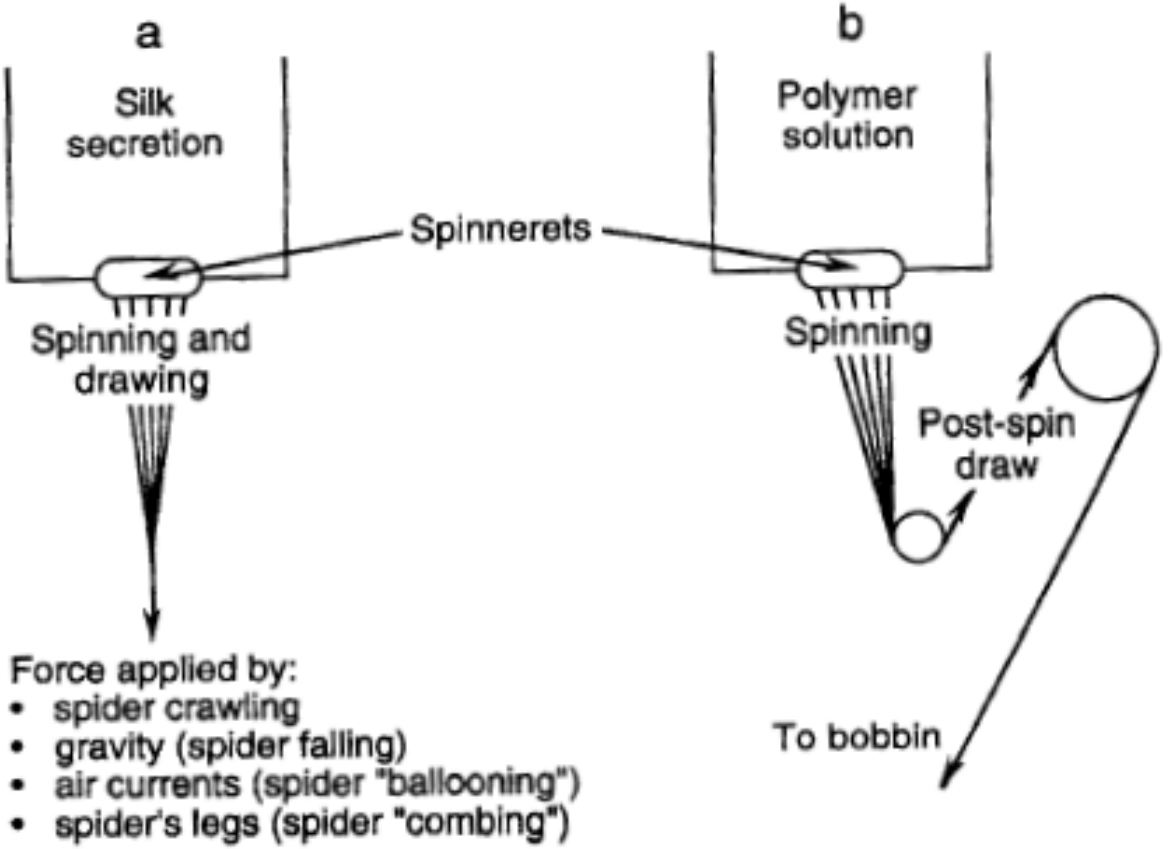
- **Achniform gland**: swathing silk
- **Cylindriform gland**: egg sac silk.
- **Ampullate glands (major and minor)**: non-sticky dragline silk. Silk from the minor ampullate gland is only half as strong as that from the major gland.
- **Pyriform gland**: attaching threads - attachment discs are made which anchor a thread to a surface or another thread.
- **Flagelliform gland**: core fibers of sticky silk.
- **Aggregate gland**: outer part of sticky silk - droplets of an adhesive substance are deposited along the threads.

2. Elements of biological materials

Spinning of fibers, by spider and industrial process

Spider: simultaneous spinning and drawing

Industrial process: spinning (e.g. by extruding), then post-spin drawing



From M. Elices, 2000. Chapter 10, C. Viney.

2. Elements of biological materials

2.1.4 Collagen

Main structural protein in human body.

Fibrous protein with amino acid sequence of type $(Gly\text{-}X\text{-}Y)_n$, based on a triple helix made from 3 single alpha helices.

Types of collagen:

Type of collagen	**Type of tissue**
I	skin, tendons, bone, cornea
II	cartilage, vitreous body of the eye
III	skin, blood vessels, lymph nodes
V	skin, tendons, muscles, cornea
XI	cartilage

Collagen I: 2 identical alpha helices, 3rd chain different
Collagen III: 3 identical alpha helices

2. Elements of biological materials

Amino acid composition of collagen

Table 2.6 Amino acid composition (%) of rat tail tendon

Ala	9.9	Thr	1.9
Gly	35.1	Met	0.6
Val	2.3	Arg	4.7
Leu	2.2	His	0.3
Ile	1.3	Lys	3.6
Pro	12.3	Asp	4.7
Phe	1.4	Glu	7.4
Tyr	0.5	Hyp	9.0
Ser	2.8		

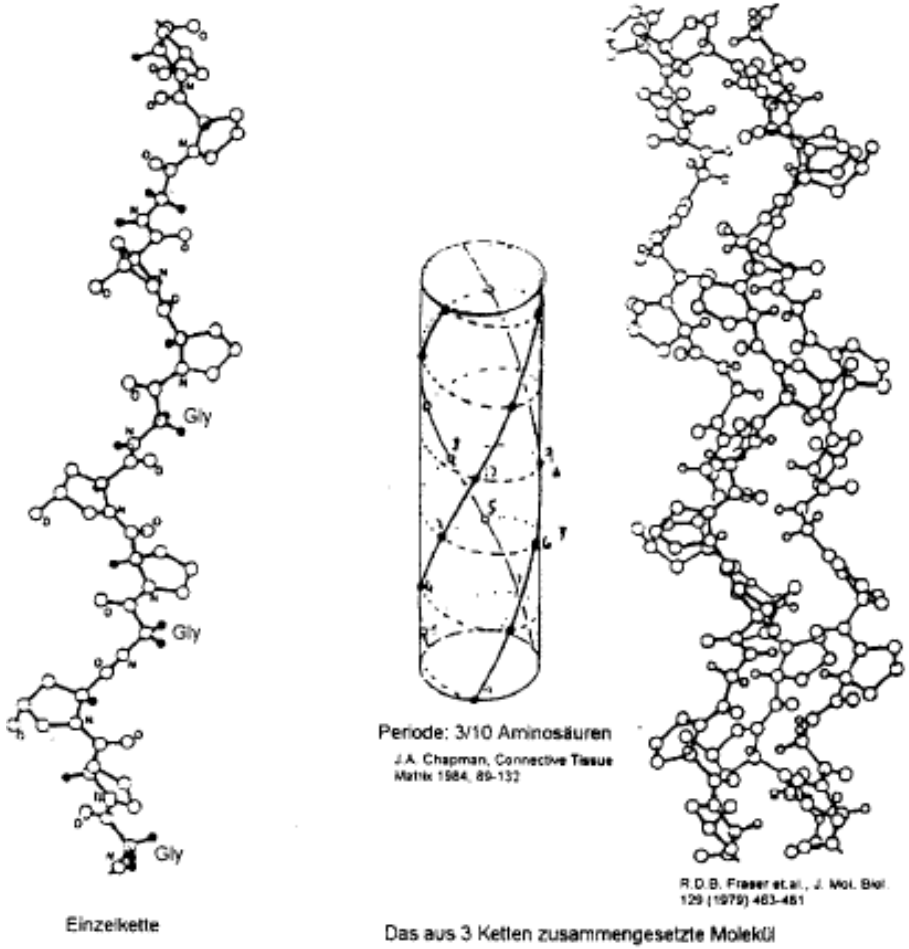
From Brown (1975)

Helix breakers or helix formers?

2. Elements of biological materials

Secondary structure of collagen

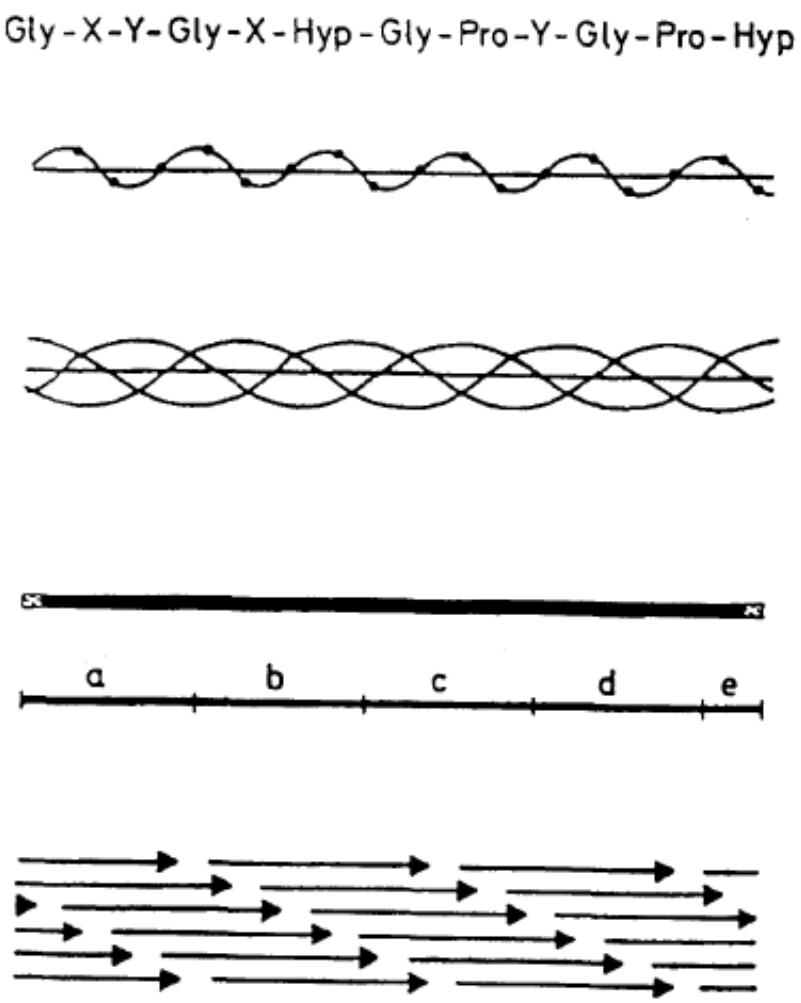
Left-handed alpha helix



Three alpha helices combine into a triple helix (collagen molecule)

2. Elements of biological materials

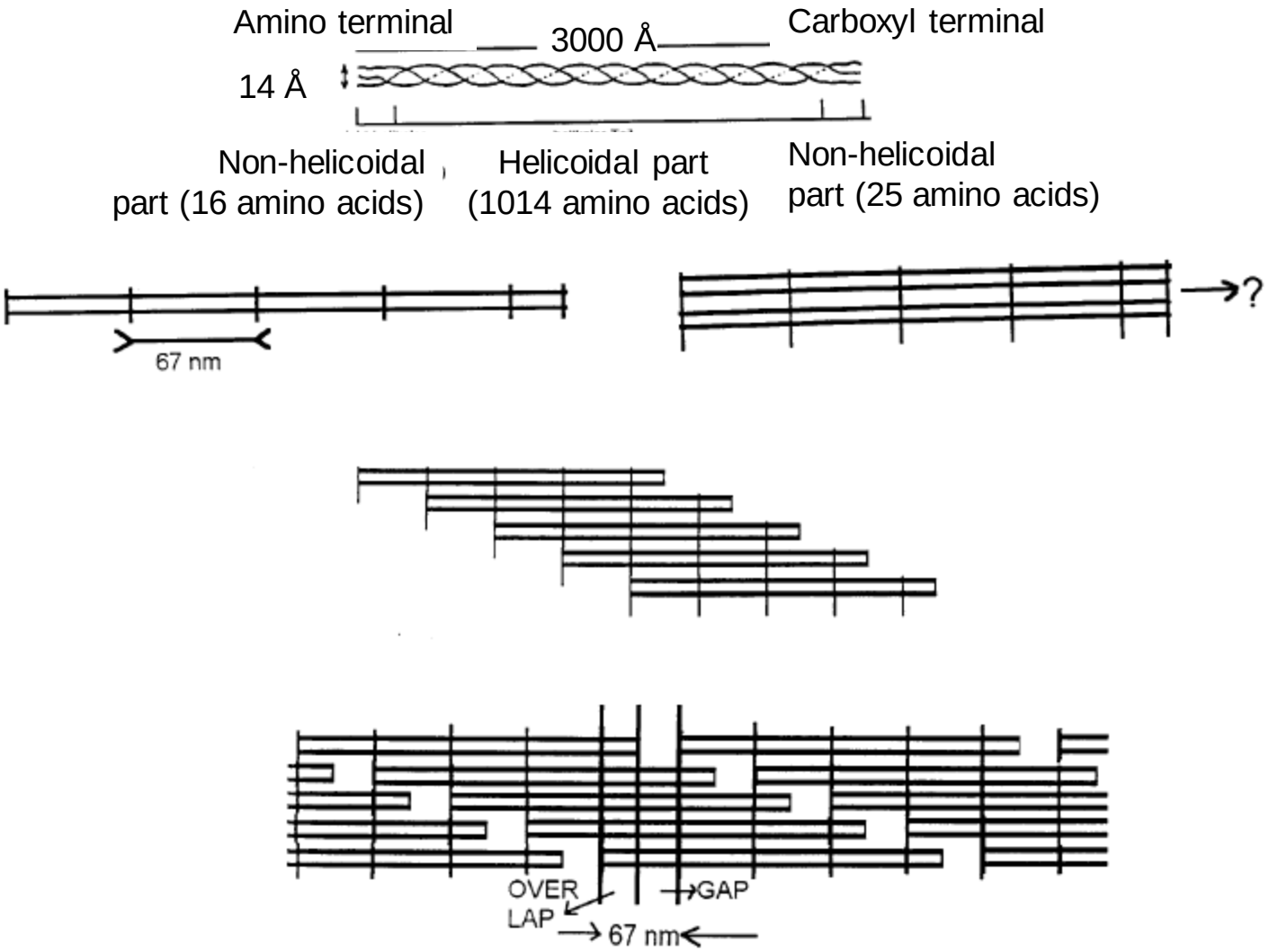
Structural levels of collagen



2. Elements of biological materials

Stacking of collagen molecules

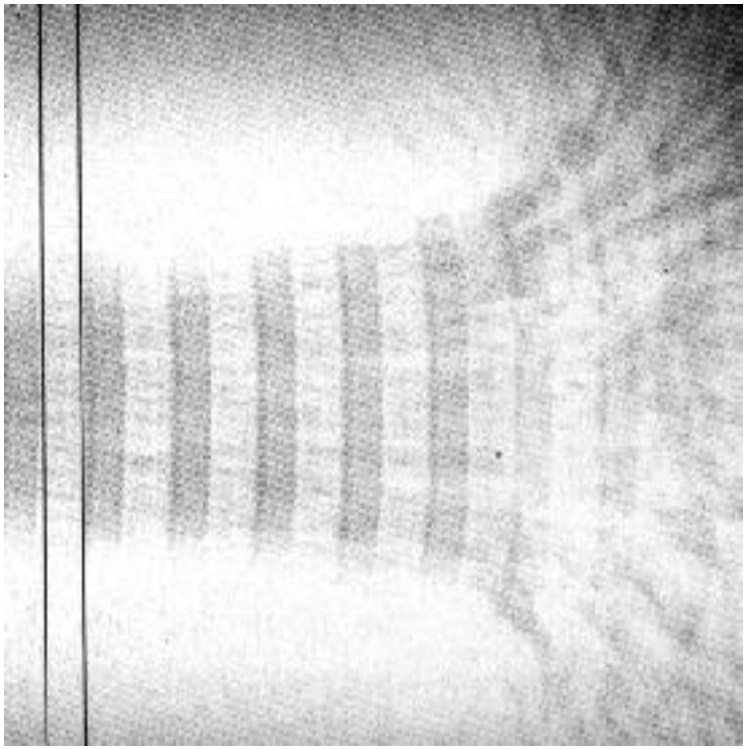
How to obtain a stable fiber in 3D



2. Elements of biological materials

Gap and overlap structure of collagen fiber

sketch



TEM – image

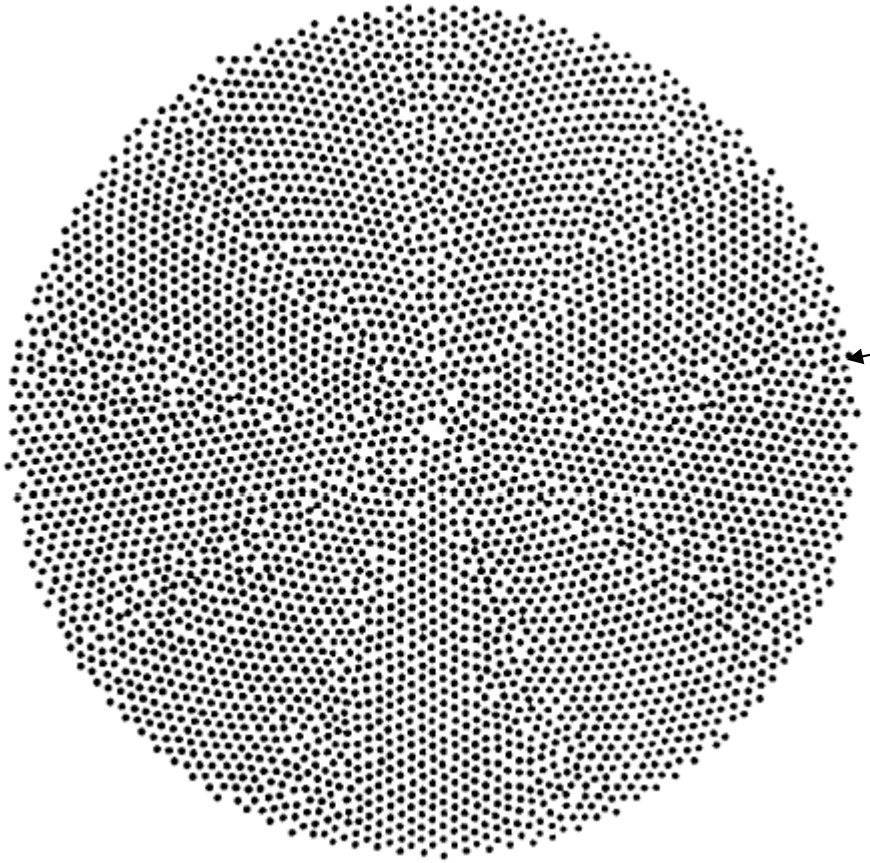
macro-period: D= 67 nm, overlap zone: 0.4 D

2. Elements of biological materials

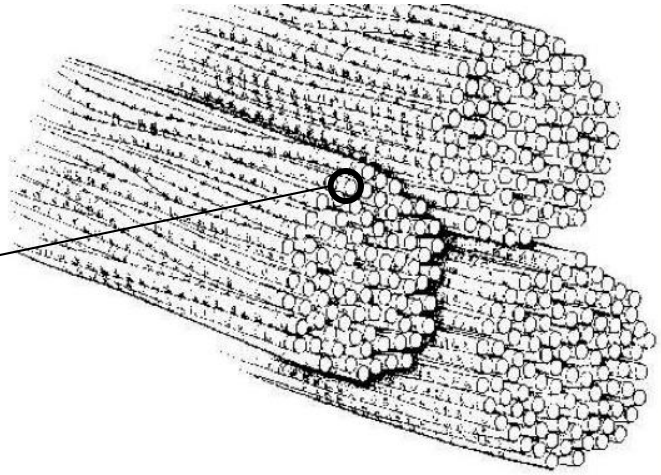
Cross section of collagen fibril

Arrangement of collagen molecules in cross section:

quasi-hexagonal packing



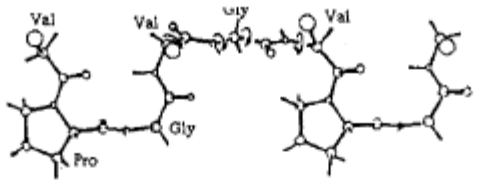
collagen fiber bundle



Further agglomeration of collagen fibrils into collagen bundles.

2. Elements of biological materials

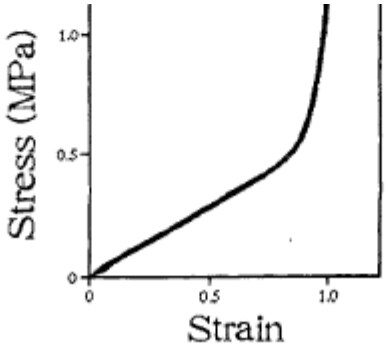
2.1.5 Protein rubbers



e.g. elastin

β-turn of elastin, showing the rotations which lead to the elastic properties (Urry 1983). *From J. Vincent, 1990.*

Assembly of β-turns into the primary elastin helix which is further assembled into fibers (Urry 1983). *From J. Vincent, 1990.*



Stress-strain curve for ligamentum nuchae (Dimery *et al.* 1985). *From J. Vincent, 1990.*

2. Elements of biological materials

Summary, structural proteins

Keratin:

•hair keratin: 2 alpha helices, contains cysteine (forms disulphide bonds -> hairstyling)

•feather keratin: made from beta-sheets

Silk:

•silkworm silk: mostly Ala and Gly (regular sequence); sheet-like arrangement

•spider silk: high strength and toughness, partly crystalline;
spinning and drawing process at the same time -> water soluble precursor, water-insoluble final product

Collagen:

typical sequence: (Gly-X-Y)n

triple helix

regular stacking of collagen molecules -> gap-overlap zones

associates to collagen fibrils

2. Elements of biological materials

2.2 Polysaccharides

Chains of sugar molecules

Structural polysaccharides:

Fibrous polysaccharides:

- cellulose (plants)
- chitin (insects)

Sugars as fillers:

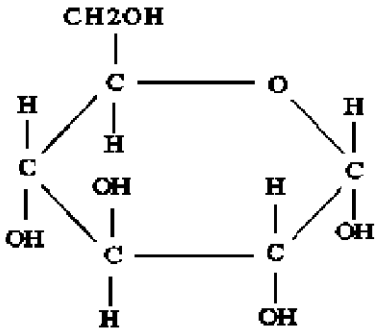
- lubricant in joints
- polysaccharide gels as shock absorber

Energy storage
etc.?

2. Elements of biological materials

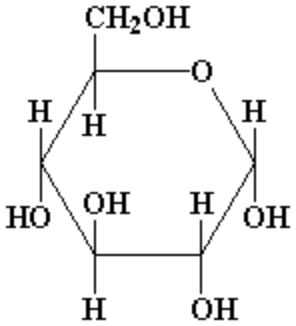
Monosaccharides

Glucose: $C_6H_{12}O_6$



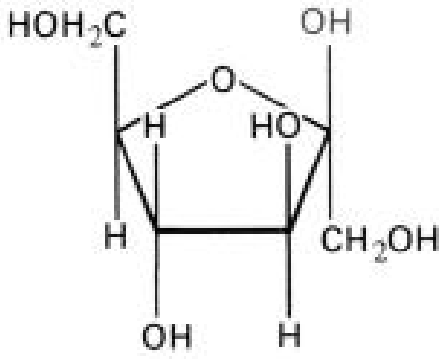
Glucose

or



glucose

Fructose: $C_6H_{12}O_6$

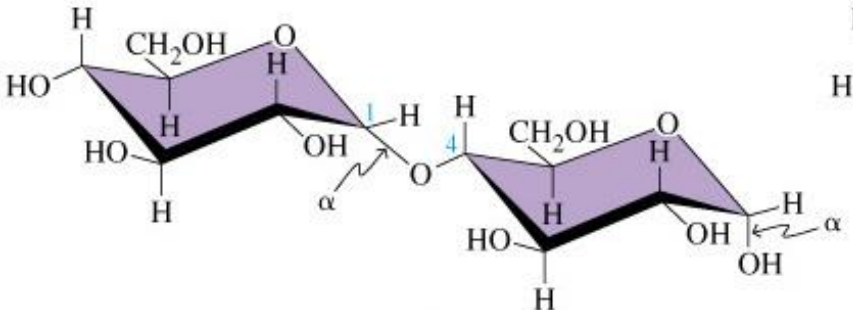


β-Fructose

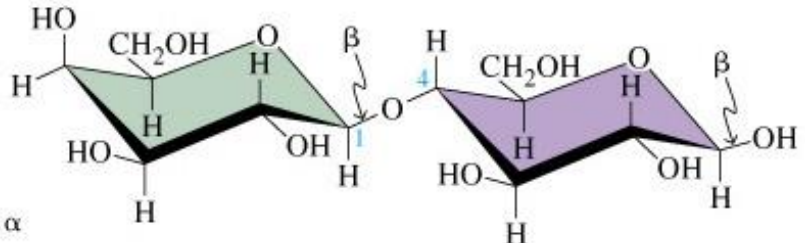
General formula (for most monosaccharides): $C_xH_{2x}O_x$

2. Elements of biological materials

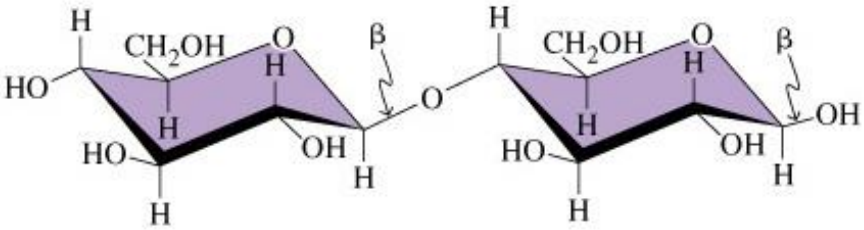
Disaccharides



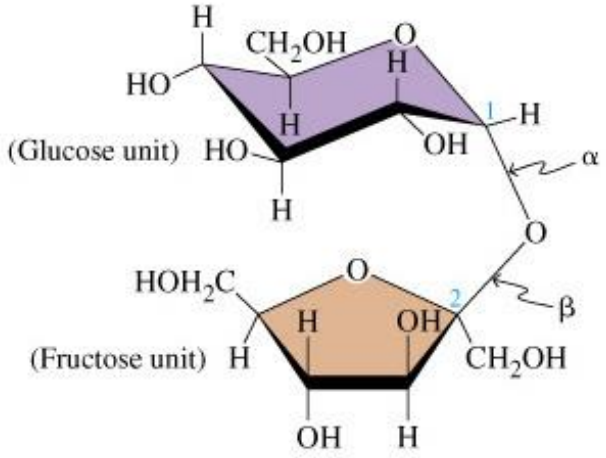
Maltose (α form)



Lactose (β form)



Cellobiose



Sucrose

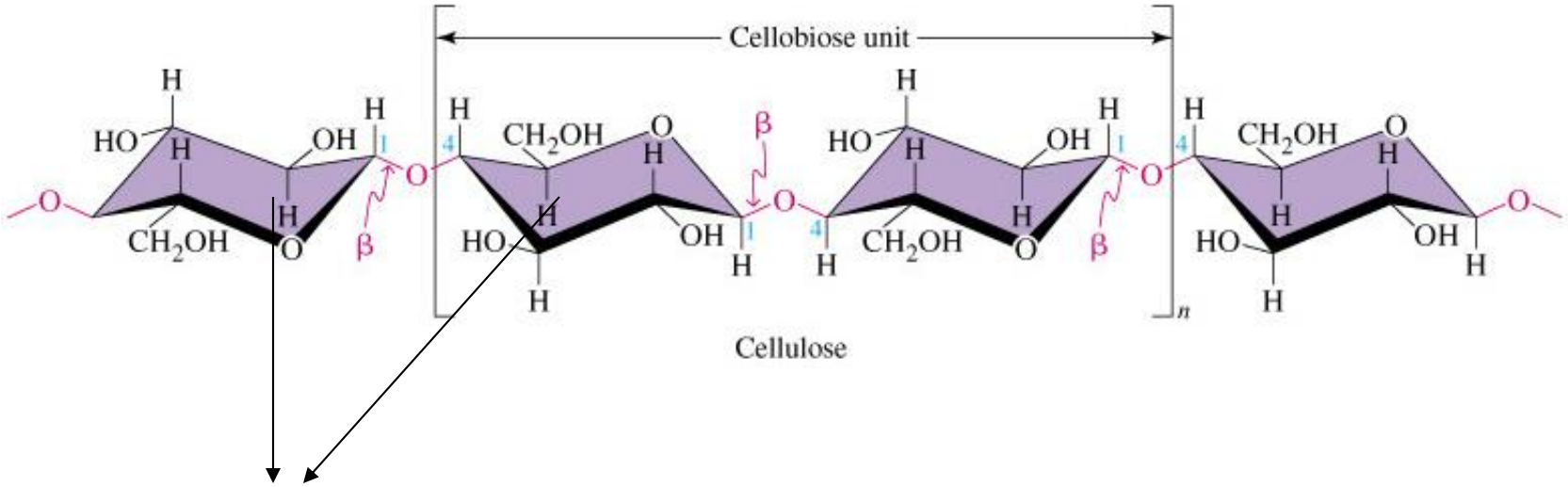
Glucose *Galactose* *Fructose*

2. Elements of biological materials

2.2.1 Cellulose

Consists of cellobiose (beta-D-glucose)

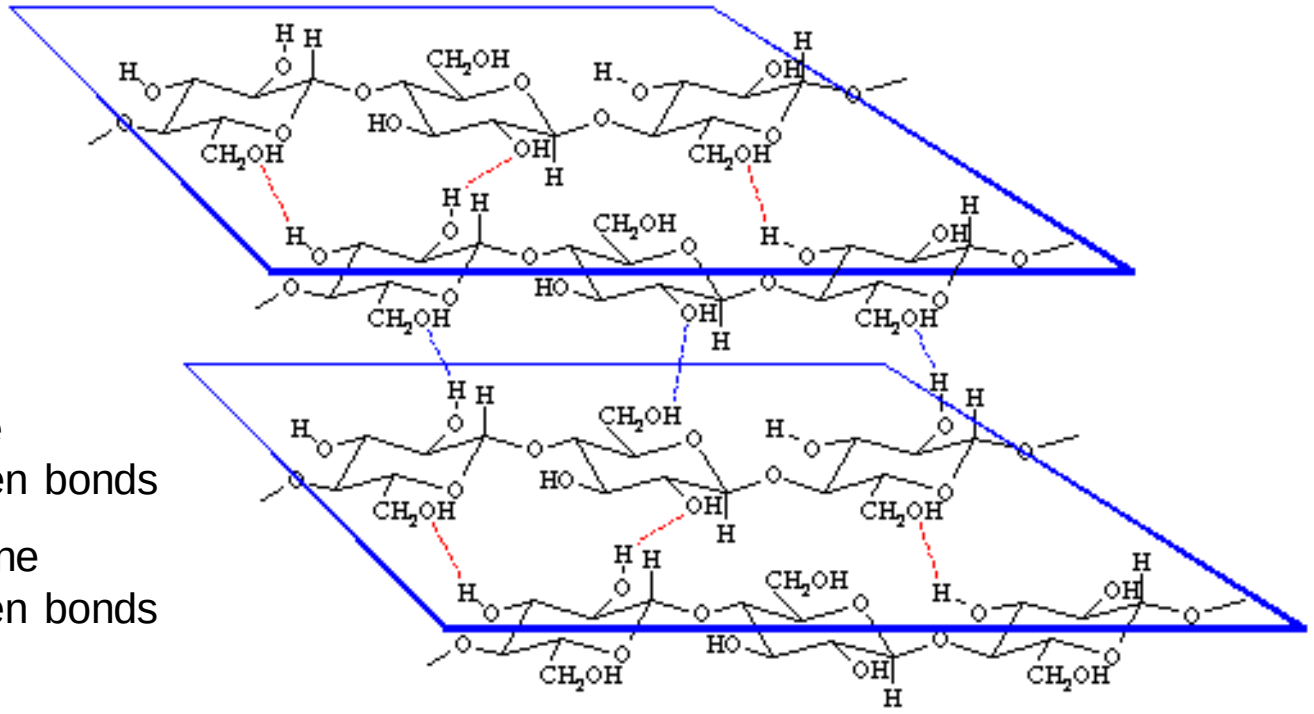
Molecular structure of cellulose:



2. Elements of biological materials

Arrangement of cellulose molecules

Adjacent chains linked by hydrogen bonds, planes linked by hydrogen bonds -> regular arrangement, cellulose crystal



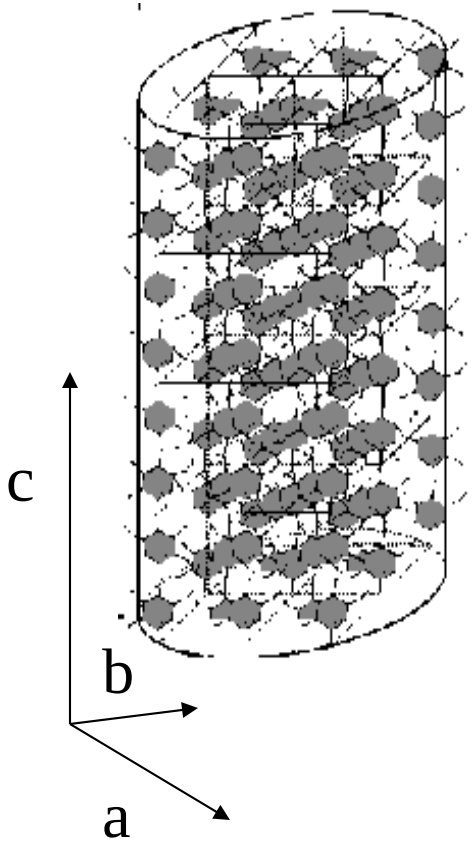
In-plane hydrogen bonds

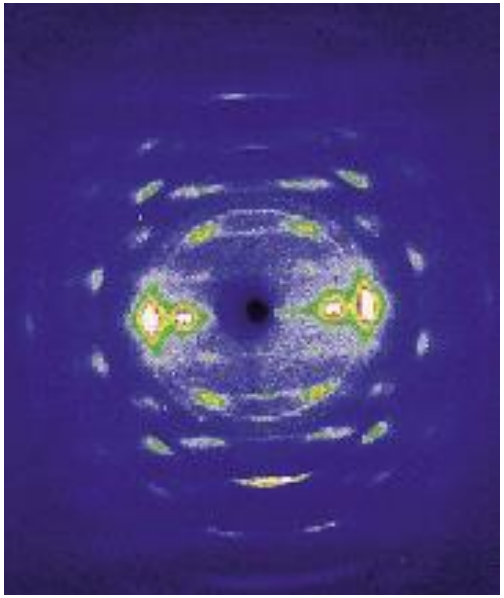
Interplane hydrogen bonds

2. Elements of biological materials

Crystalline cellulose fibrils

Crystal structure of cellulose can be verified by x-ray diffraction.

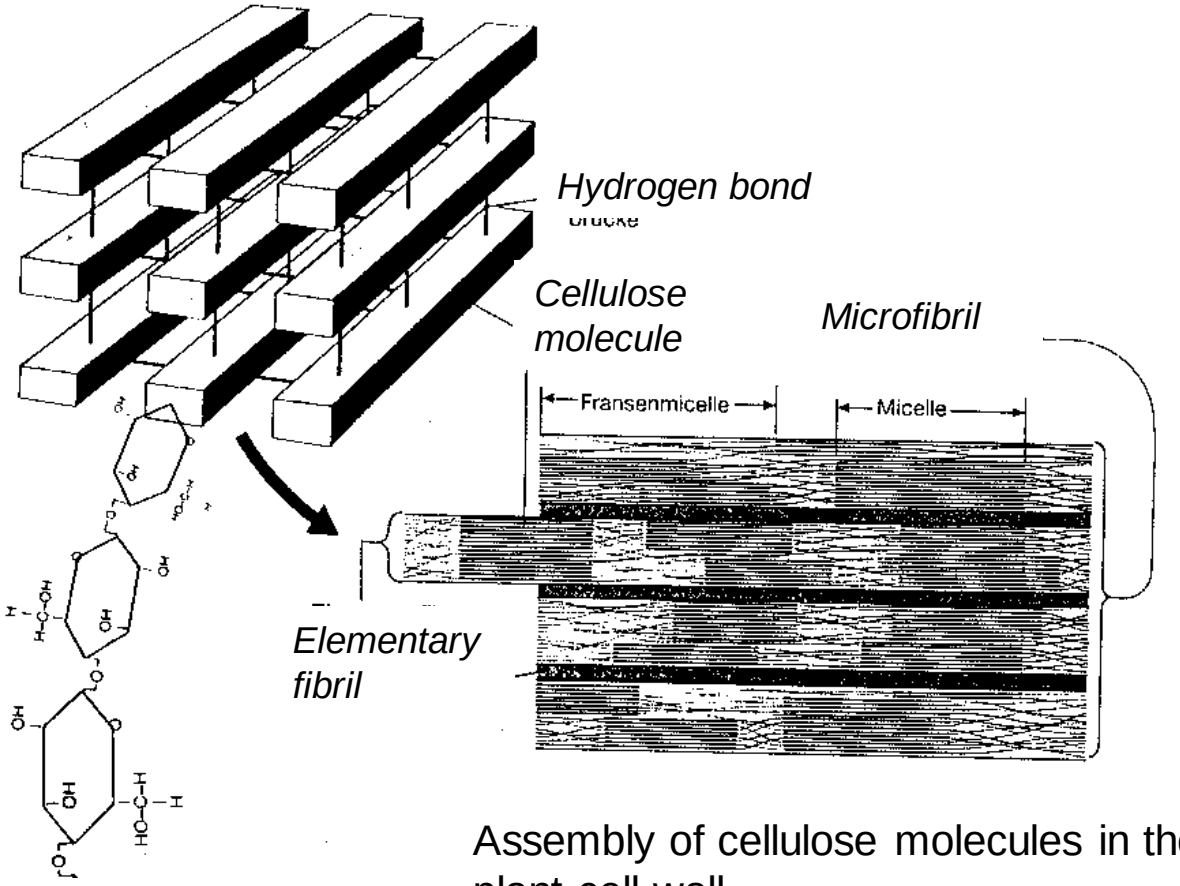




Synchrotron XRD pattern

2. Elements of biological materials

Arrangement of cellulose in fibrils



Assembly of cellulose molecules in the plant cell wall

From Lüttge et al.: Botanik, 2nd Edition, VCH, 1994.

2. Elements of biological materials

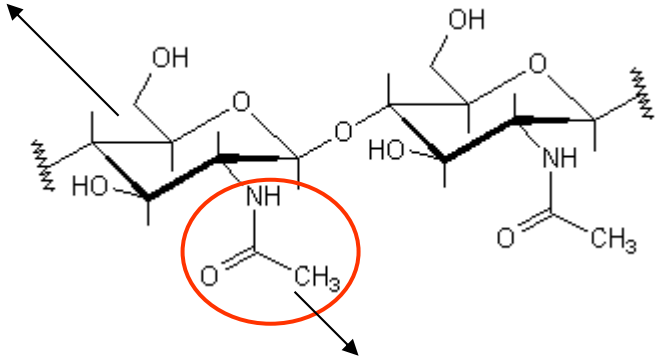
2.2.2 Chitin

Chitin is a polysaccharide very similar to cellulose, but with different side group.

Chitin occurs in insect tissue.

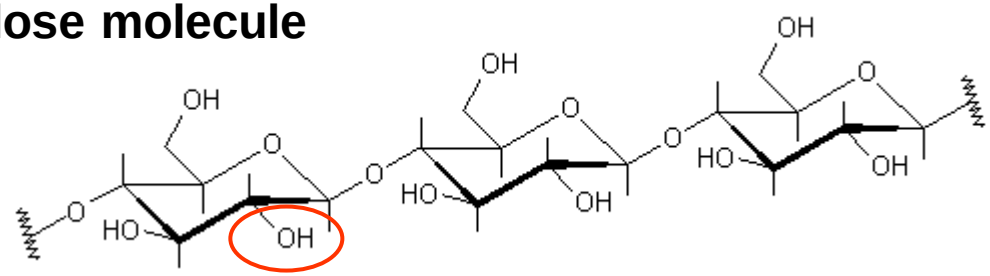
Chitin molecule

acetylglucosamine



actetylamine group

Cellulose molecule

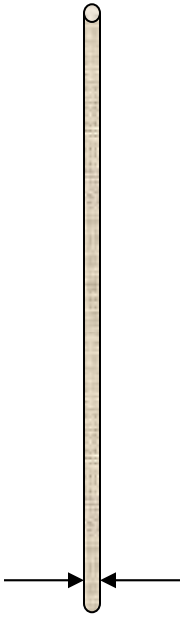


2. Elements of biological materials

Cellulose and chitin fibers

Both, cellulose and chitin naturally occur as fibers. Similar dimensions and similar stiffness:

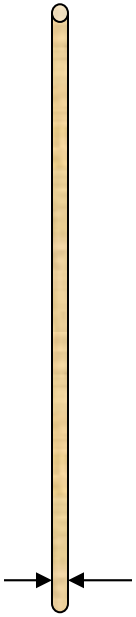
Cellulose fibril



2-100 nm

E = approx.140 GPa

Chitin fibril



approx. 3-300 nm

E>140 GPa

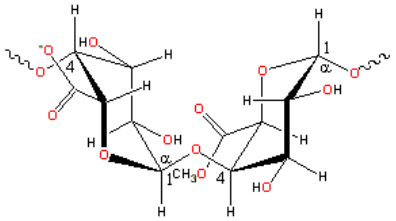
(Compare: steel E=210 GPa)

2. Elements of biological materials

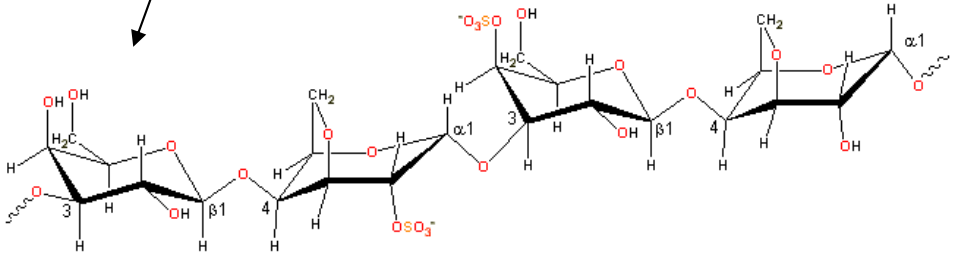
2.2.3 Polysaccharides as fillers

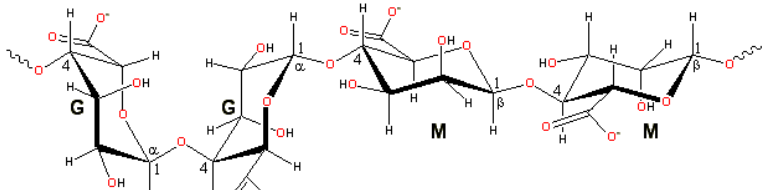
Many polysaccharides occur as fillers, often in form of a polysaccharide gel.

Pectins (from fruit): form lubricating gels or glues

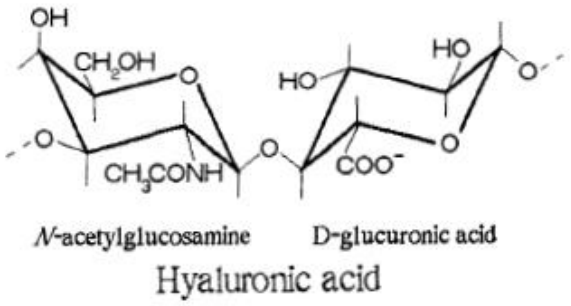


Carageenans and alginates (gels extracted from dried seaweed)





Hyaluronic acids (in synovial fluid, cartilage....



etc.

2. Elements of biological materials

Summary Polysaccharides

Polysaccharides are chains of sugars

Cellulose:
found in plant cell walls;
consists of cellobiose units (disaccharide from 2 glucose units);
cellulose molecules associate to build crystalline cellulose fibrils;

Chitin:
found in insect cuticle;
consists of acetylglucosamine units (otherwise similar to cellulose);
molecules associate to build stiff fibrils

Polysaccharide gels: pectin, carrageenan, alginates, hyaluronic acid, etc.

3. Self assembly and growth

Definition of self-Assembly

Self-Assembly denotes the spontaneous formation of organized structures by a stochastic process involving pre-existing components, is reversible and controlled by appropriate design of the components, the environment and driving forces.

J. A. Pelesko, The Science of Things that Put Themselves Together, Chapman and Hall 2007

3. Self assembly and growth

History

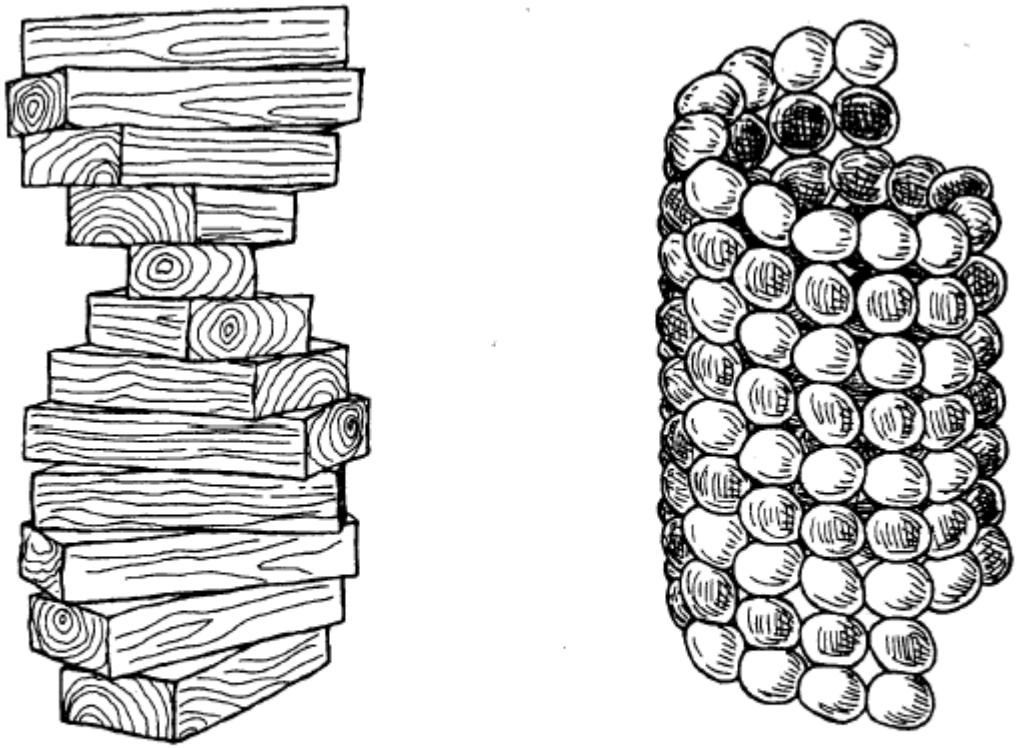
- **1950** Horace Richard Crane predicted the many biological structures must be helical
- **1953** James D. Watson, Francis Crick, Maurice Wilkins and Rosalind Franklin discover the double helix structure of the DNA
- **1955** Self-assembly of a tabacco mosaic virus (TMV) in a test tube (H. Fraenkel-Conrat und R.C. Williams)
- **1962** First mathematical model for the description of self assembly (F. Oosawa und M. Kasai)

Since then strongly increasing interest from a variety of discipilines: biology, biochemistry, biophysics, materials science, etc.

3. Self assembly and growth

Helix

Simplest example of a stable, self-assembled structure:



A helix of identical wooden blocks and a model of a microtubule. The latter has thirteen elements per turn, each consisting of a pair of protein molecules. In either case each element is in a position equivalent to that of every other. *From S. Vogel, 1998.*

3. Self assembly and growth

3.1 Basic principles of self-assembly

Forces involved in self assembly: mostly weak forces!

Attractive:

- Van der Waals forces
- Attractive electrostatic forces in solution
- Hydrophobic interaction
- Hydrogen bonds

Repulsive:

- Steric repulsion
- Repulsive electrostatic forces in solution
- Hydration forces in water

Aus Y.S. Lee, Self Assembly and Nanotechnology, Wiley (2008)

3. Self assembly and growth

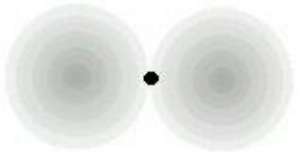
Strong forces

Covalent bond, atoms share pair(s) of electrons, e.g HCl

H

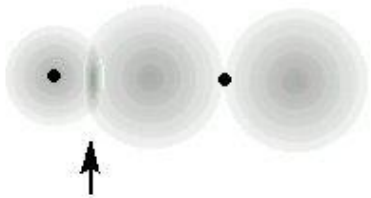
Hydrogen atom
1s orbital ($1s^1$)

Cl



Chlorine atom
3p orbital
($1s^2 2s^2 2p^6 3s^2 3p^5$)

HCl



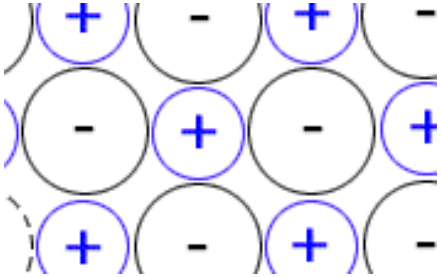
Overlap of hydrogen 1s
and chlorine 3 p orbitals

Binding energy: approx. 4000 meV / bond

Elektrostatic interaction

(ionic bond, z.B. ionic crystal NaCl)

Binding energy: approx. 5000 meV / bond



1 eV=1.6 x 10^{-19} Joule

3. Self assembly and growth

Hydrogen bonds

Example water: greater electron affinity of oxygen (O) → shared electron pair is located close to oxygen rather than hydrogen (H).

This leads to differences in charge distribution.

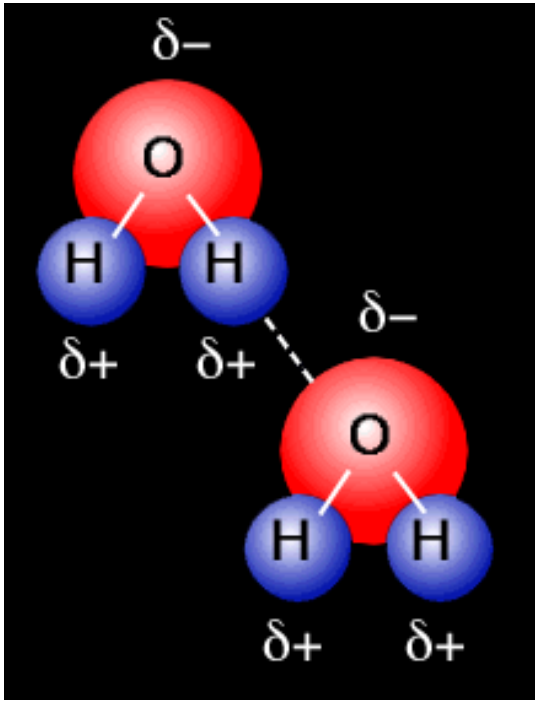
Binding energy: approx. 100-500 meV

Typical electronegative binding partners: F, N, O

H… F

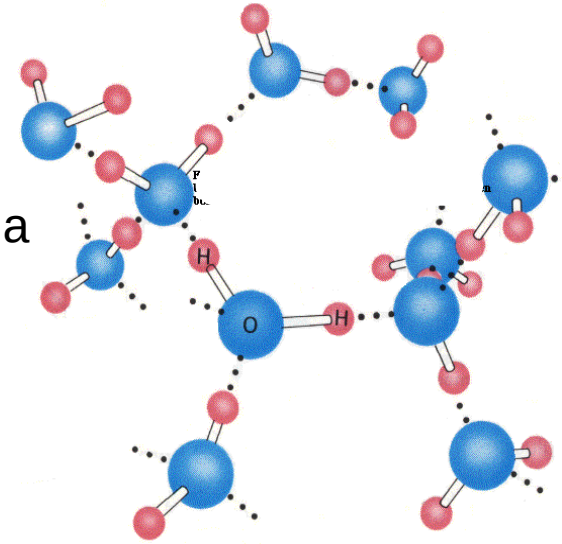
H… N

H… O



3. Self assembly and growth

Hydrophilic- hydrophobic interaction

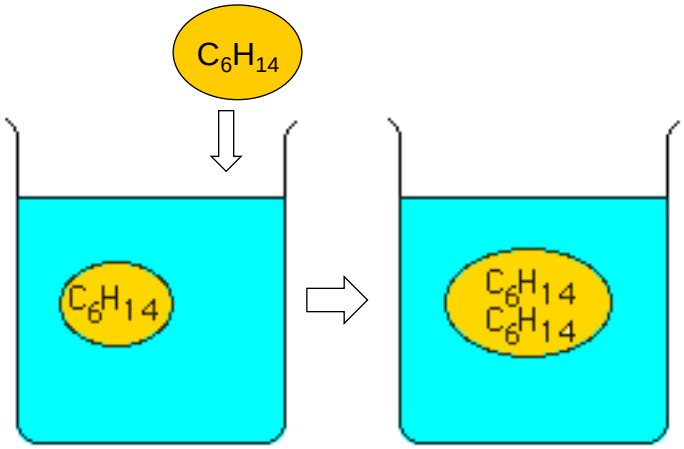


Entropy effect:

Water molecules form a dense network, can arrange in a variety of ways.

At interface to water insoluble, non-polar (hydrophobic) substance possibilities are greatly reduces → entropy decreases!

In order to keep entropy high, minimization of interface: hydrophobic interaction (e.g. separation of oil in water)



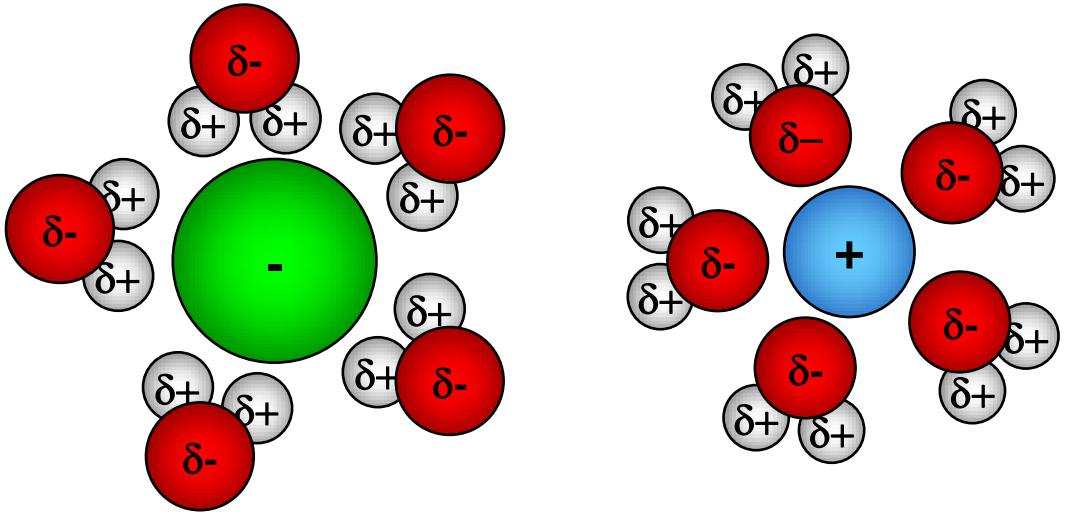
z.B. Hexane in water

3. Self assembly and growth

Electrostatic interaction in solution

Charged atoms / molecules in water

Electrostatic interaction is reduced by shielding of ions by polar water molecules.



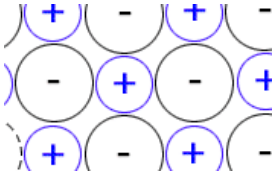
Counterfield by water molecules

(Debye-Hückel Theory)

Binding energy: approx. 100-300 meV

Compare with ionic crystal:

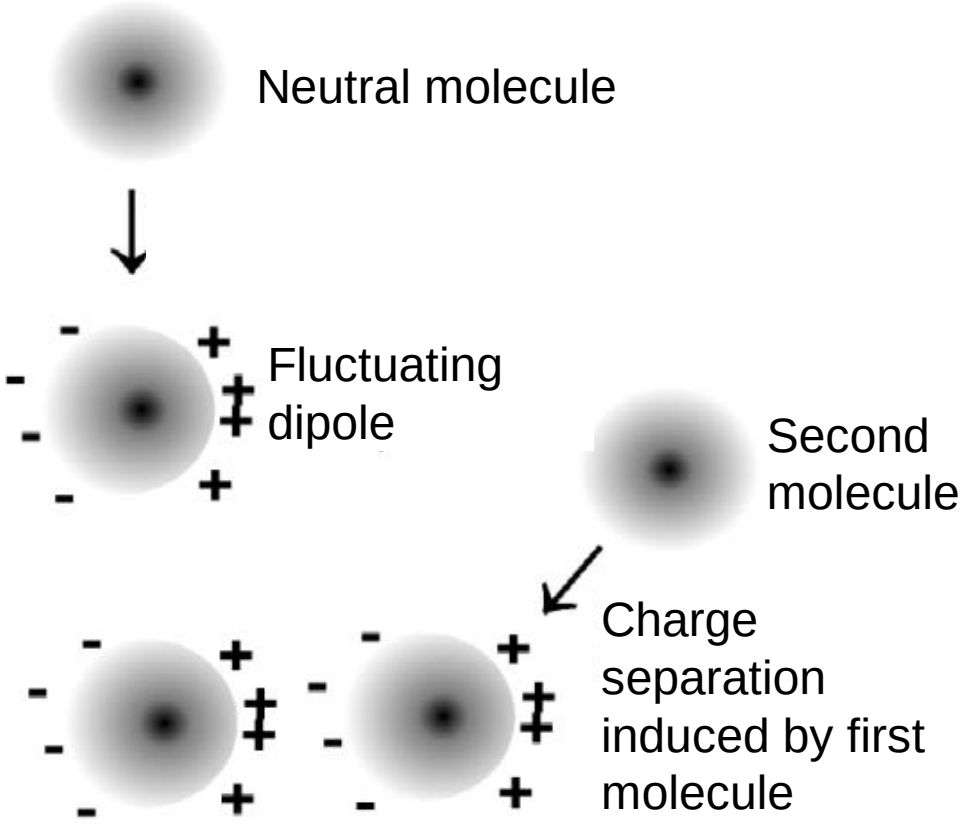
Binding energy: approx. 5000 meV

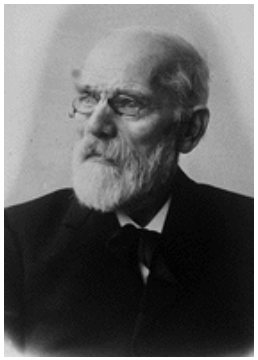


3. Self assembly and growth

Van-der-Waals interaction

Weak, short ranged





Johannes Diderik van der Waals (1837-1923)
Nobel Prize Physics 1910

3. Self assembly and growth

Van-der-Waals interaction

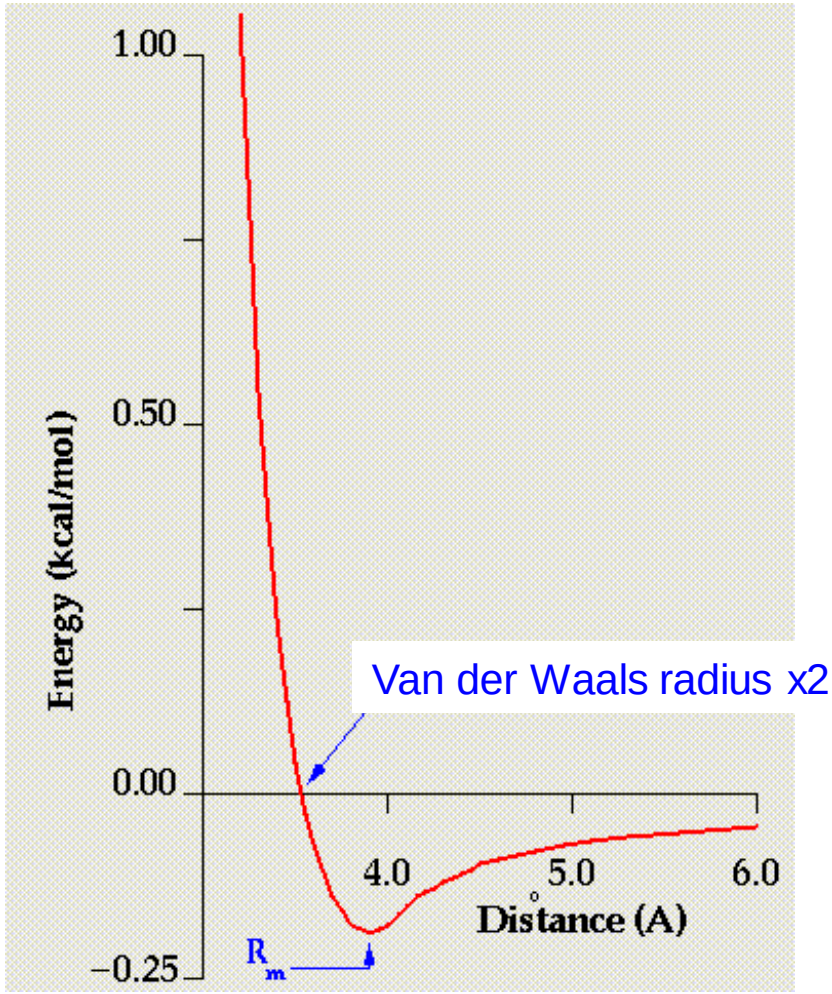
Lennard-Jones potential:

$$E_B = \frac{K_1}{r^{12}} - \frac{K_2}{r^6}$$

Van der Waals forces are considerable only for D<2a+a/8

a=diameter of molecule

D=distance



Binding energy: approx. 5-50 meV

3. Self assembly and growth

Binding energies

Bond	Binding energy [meV/bond]	Boltzmann factor at 20°C
Covalent	approx. 4000	10^{-69}
Electrostatic, in vacuum	approx. 5000	10^{-87}
Hydrogen bond	100-500	0,01 - 10^{-9}
Electrostatic, in solution	100-300	0,01 - 10^{-6}
Van der Waals	5-50	0,8 - 0,14
Thermal energy at RT	25	

Boltzmann factor: $e^{-E_B / kT}$

k: Boltzmann constant

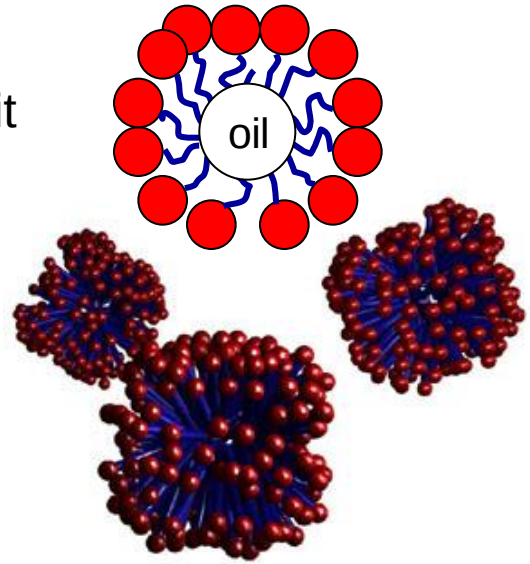
The Boltzmann factor is a measure of the probability for a molecule to have a specific thermal energy at temparature T $\rightarrow$ measure of the probability for a bond to be broken by thermal motion

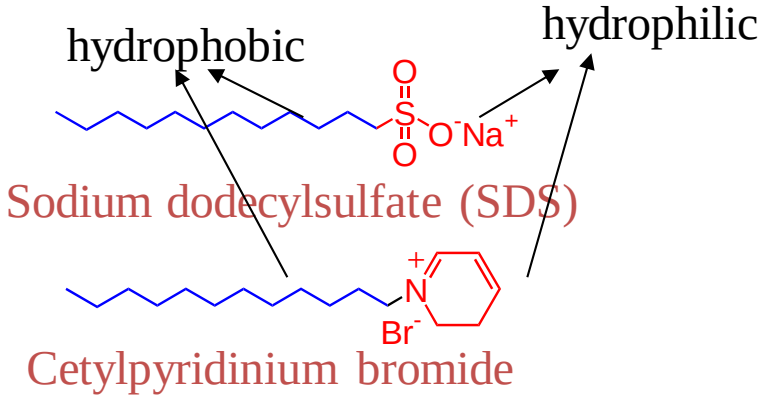
3. Self assembly and growth

Self assembly by hydrophilic-hydrophobic interaction

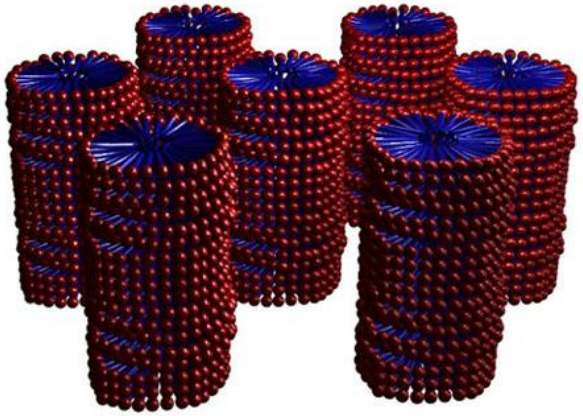
Weak, short ranged forces

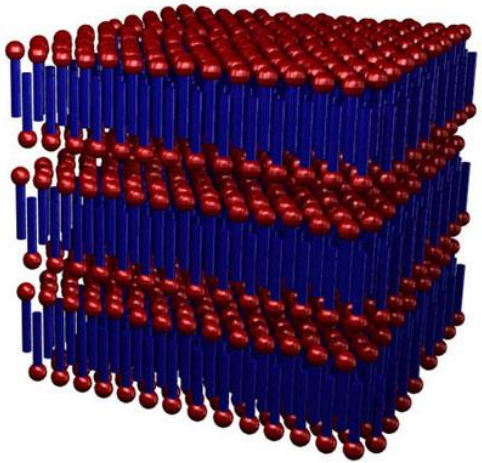
example: soap micelles: trap oil drop and screen it from water





Other possibilities: cylindrical micelles, bilayers





3. Self assembly and growth

Liquid crystalline systems

Liquid crystal (LC): state of matter in between liquid and crystal.

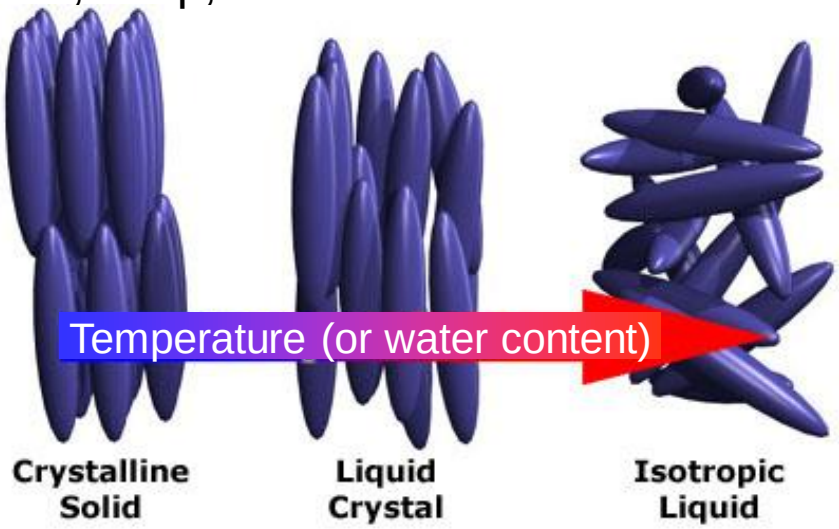
LC play an important role in biology, as intermediate stages or also final stages in self assembly (e.g. proteins, cell membranes).

History:

Discovered 1888 by Austrian botanist Friedrich Reinitzer

1991: P.G. de Gennes, Nobel Prize in physics for theory

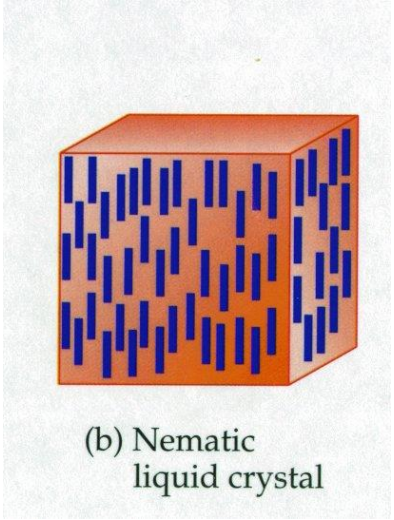
Technology today: LCD, soap, microemulsions



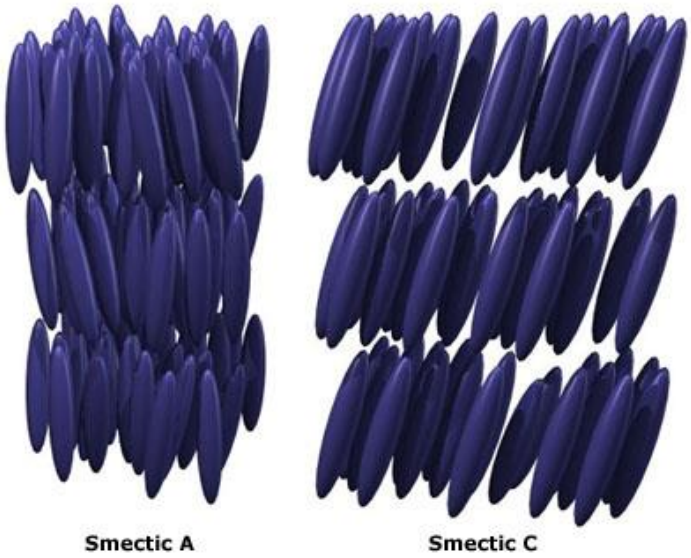
Source: http://barrett-group.mcgill.ca/tutorials/liquid_crystal/LC02.htm

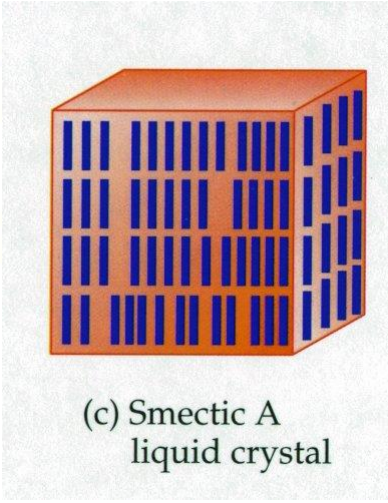
3. Self assembly and growth

Liquid crystalline phases

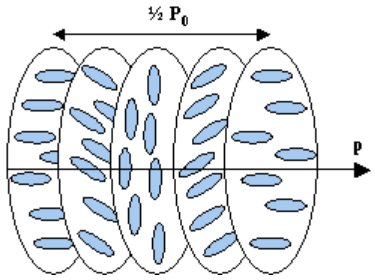


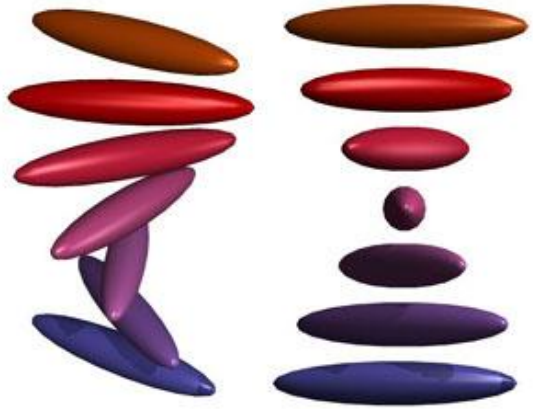
nematic





smectic

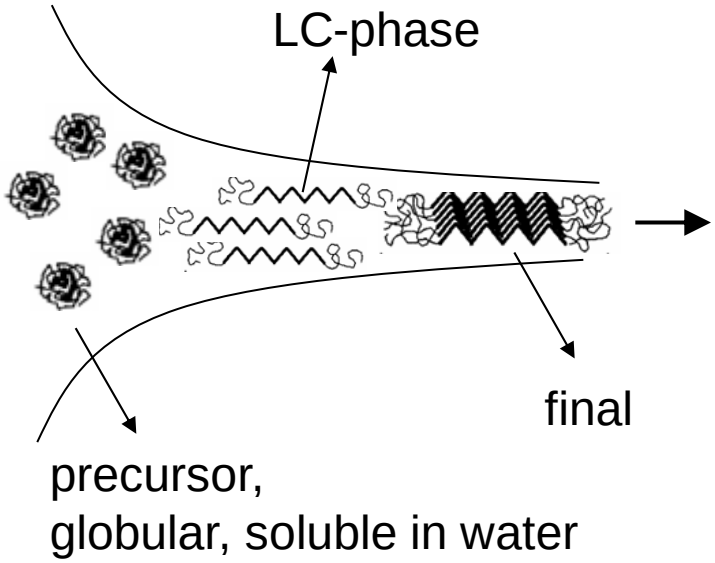


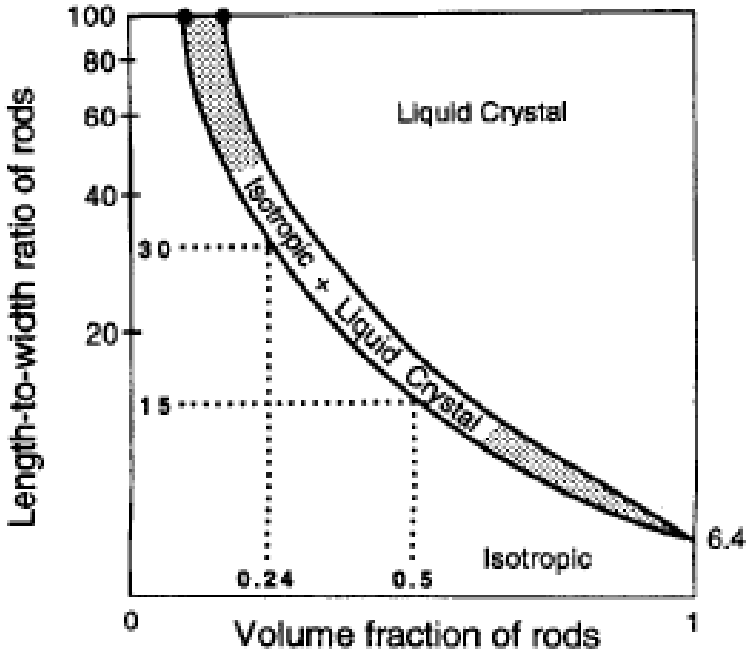


chiral nematic (cholesteric)

3. Self assembly and growth

LC Phase in spider silk production





Spider silk secretions are biphasic (isotropic + liquid crystalline phase) over a very narrow concentration range, implying „hard“ interaction of molecules (like rigid rods). Biphasic concentration depends on length / diameter ratio of rods.

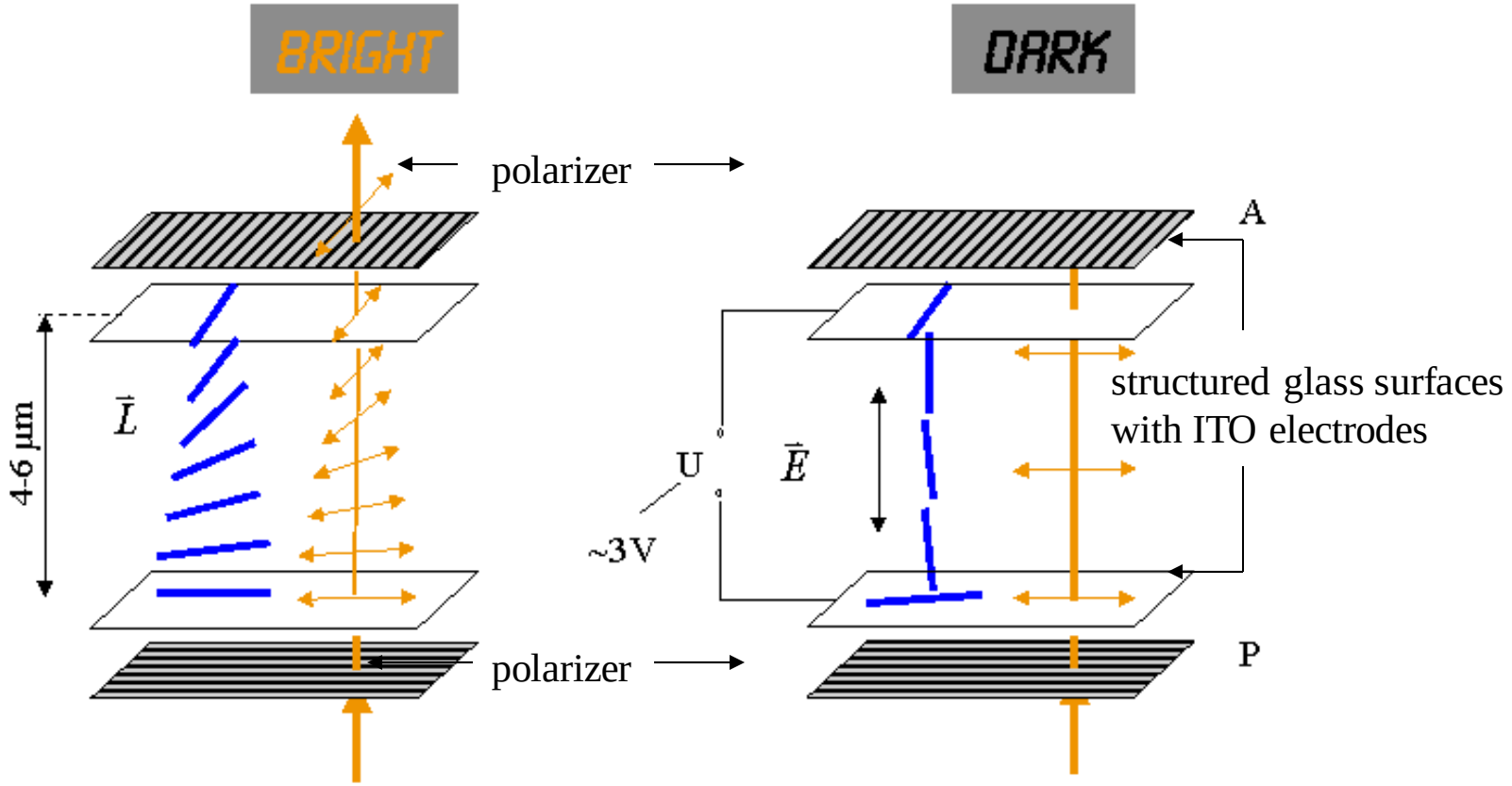
Volume fractions 24% and 50%: lower and upper bound of vol. fract. in agreement with observed density of silk and likely rod aspect ration in silk.

From M. Elices, 2000. Chapter 10, C. Viney.

3. Self assembly and growth

Technical application: liquid crystalline display (LCD)

Twisted Nematic Effect (Schadt-Helfrich effect)



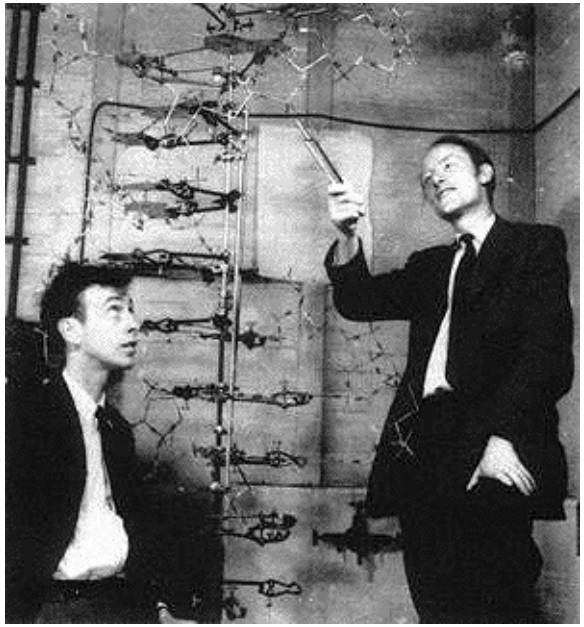
Twisted Nematic (TN) Cell

3. Self assembly and growth

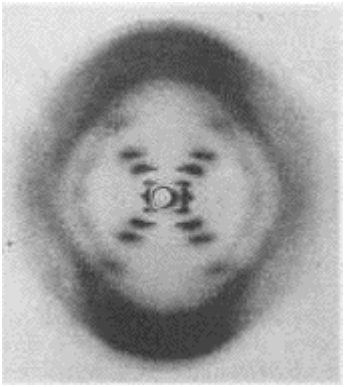
3.2 Genetic information and protein synthesis

DNA (Desoxyribonucleic acid), structure explained by:

Francis Crick James Watson Maurice Wilkins Rosalind Franklin



Nobel Prize to Crick and Watson 1962 for discovery and explanation of double-helical structure of DNA

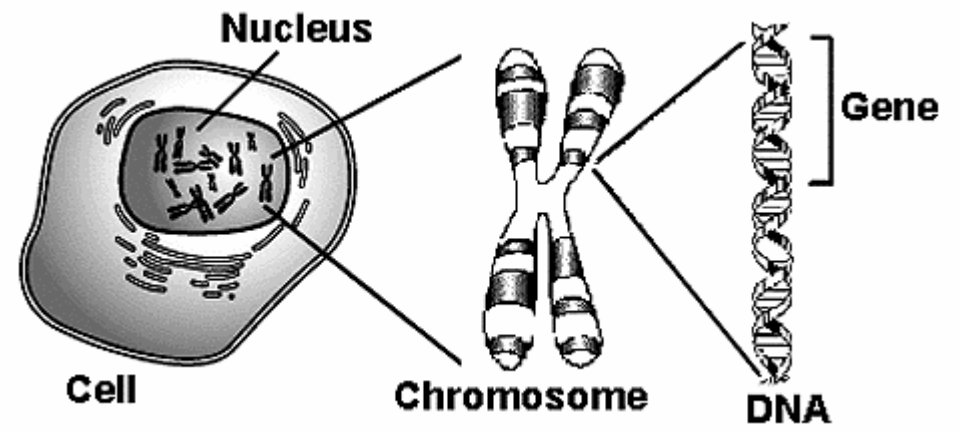


Historical X-ray diffraction image showing double helix

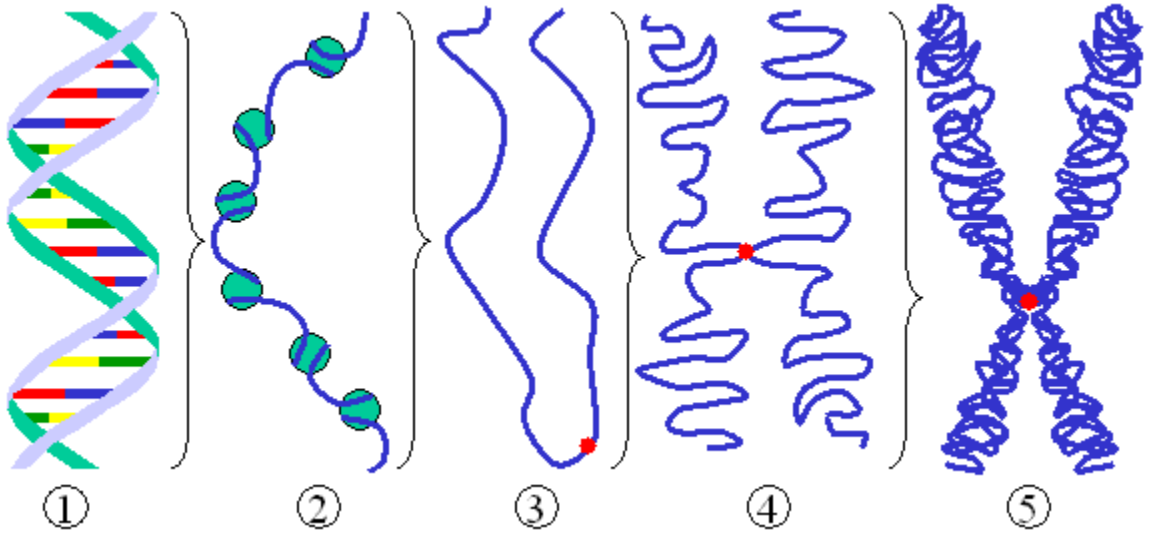
3. Self assembly and growth

Chromosomes and genes

Chromosomes contain DNA, DNA section associated with specific function: gene



Human genome:
46 chromosomes
20,000 genes?
DNA up to 5 cm long, curled up in chromosomes.



3. Self assembly and growth

Size of different genomes – complexity of organism?

Human genome: about 20,000 – 25,000 genes

Number of genes hard to tell, changes every year (new functionalities found)

Size of genome (number of base pairs)

Mammal, Homo sapiens 3×10^{9}

Nematode, Caenorhabditis elegans 8×10^{7} (roundworm)

Insect, Drosophila melanogaster 2×10^{8} (fruitly)

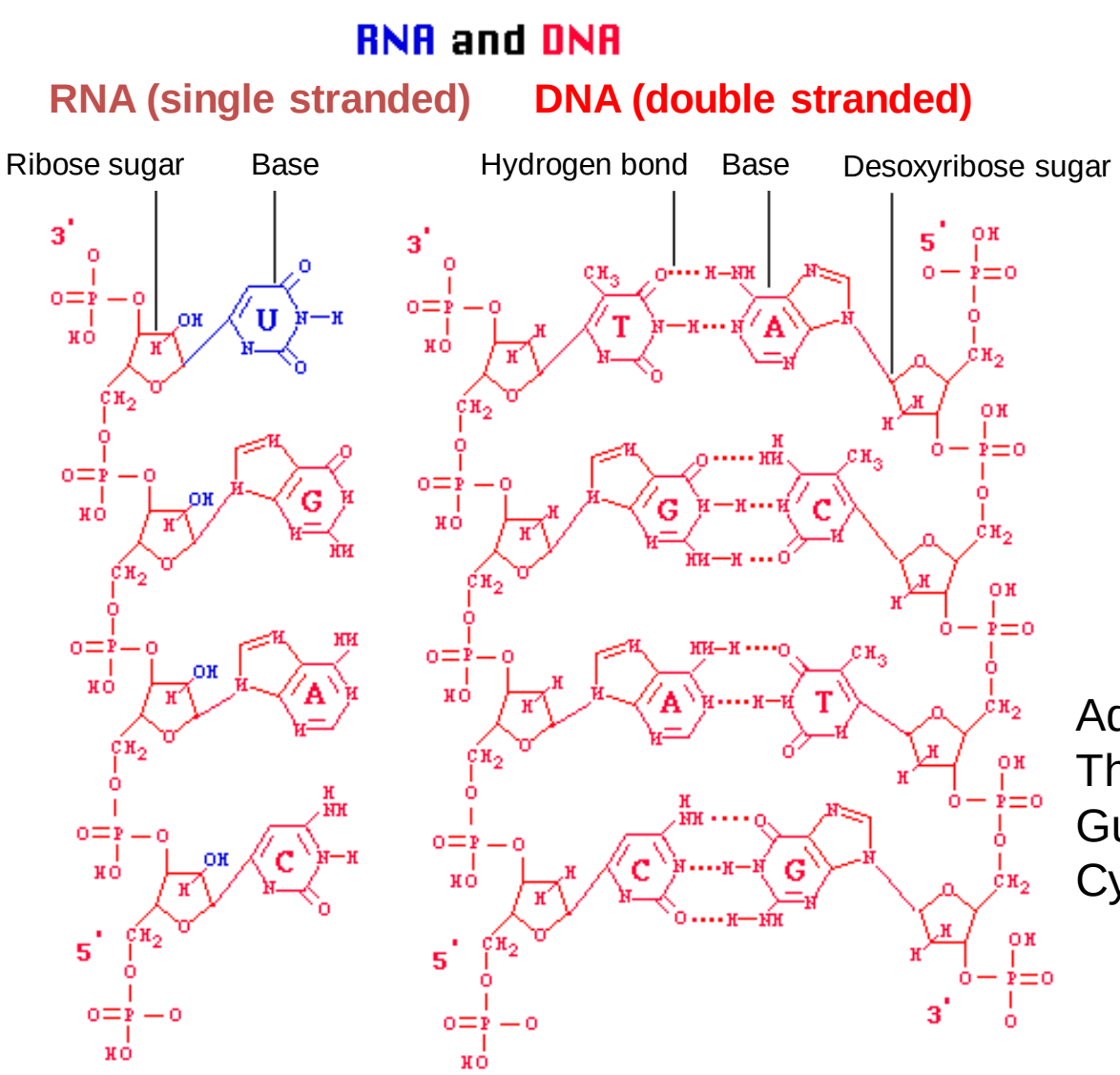
Amoeba, Amoeba dubia 6.7×10^{11} - Largest known genome

Archaeum, Nanoarchaeum equitans 5×10^{5} - Smallest non-viral genome

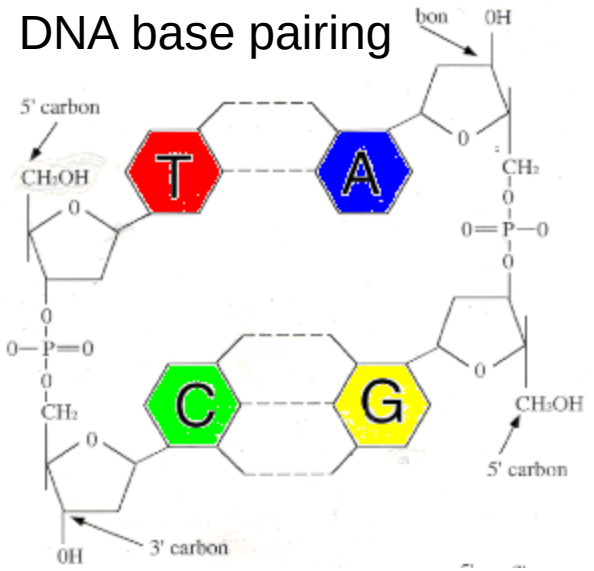
Virus, Phage Φ-X174; 5386 - First sequenced genome

3. Self assembly and growth

DNA molecule



DNA base pairing

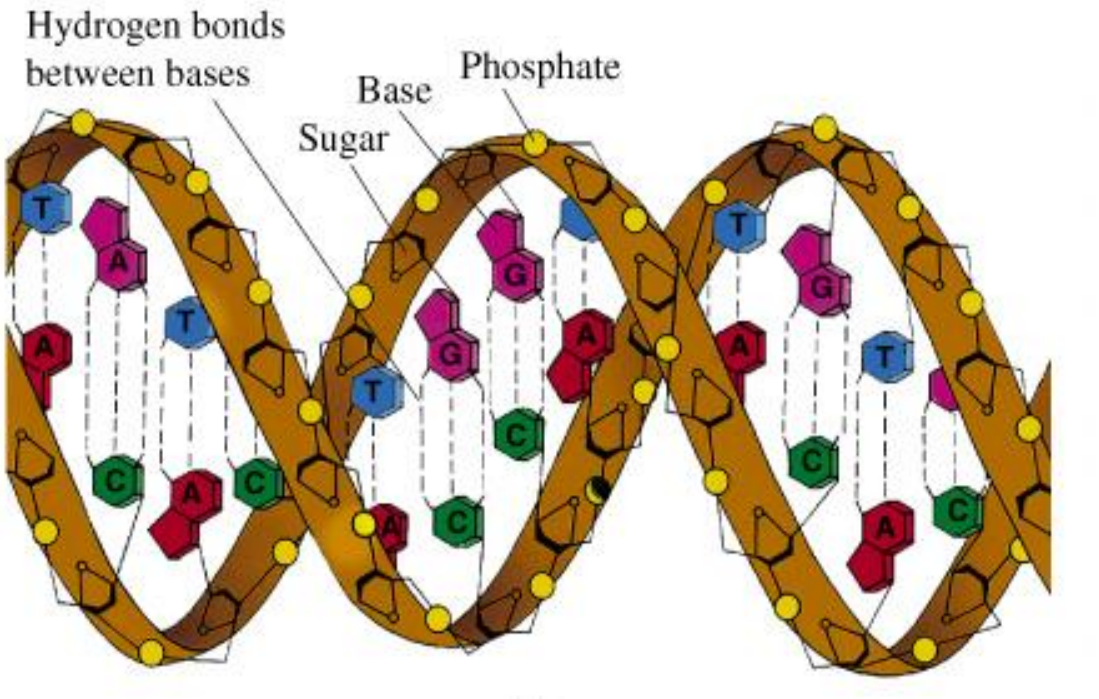


Adenine (A)
Thymine (T) – Uracil (U) in RNA
Guanine (G)
Cytosine (C)

3. Self assembly and growth

Structure of DNA

DNA is wound up to form a double helix.



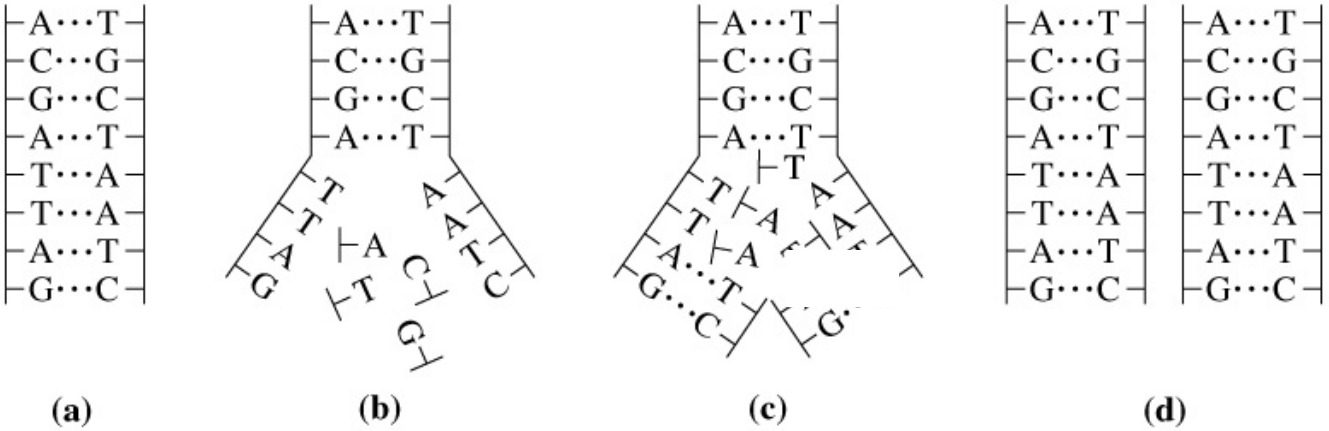
3. Self assembly and growth

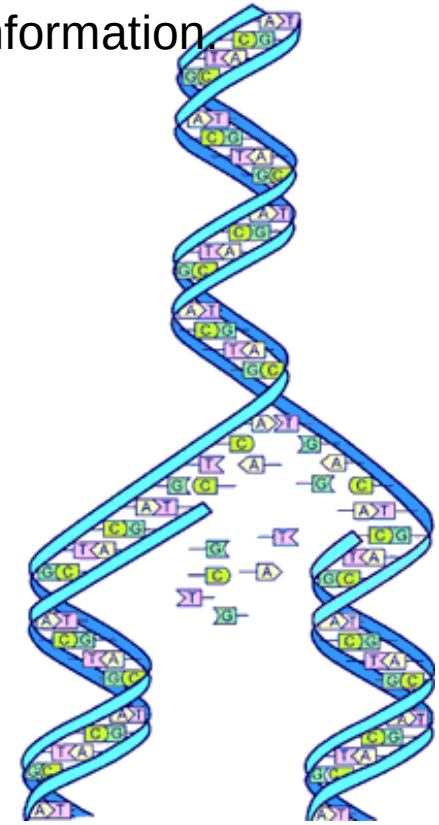
DNA replication

Process, by which information from whole DNA or sections can be copied.

Two strands of DNA are equivalent (mirror image) in terms of information

Duplication of DNA:





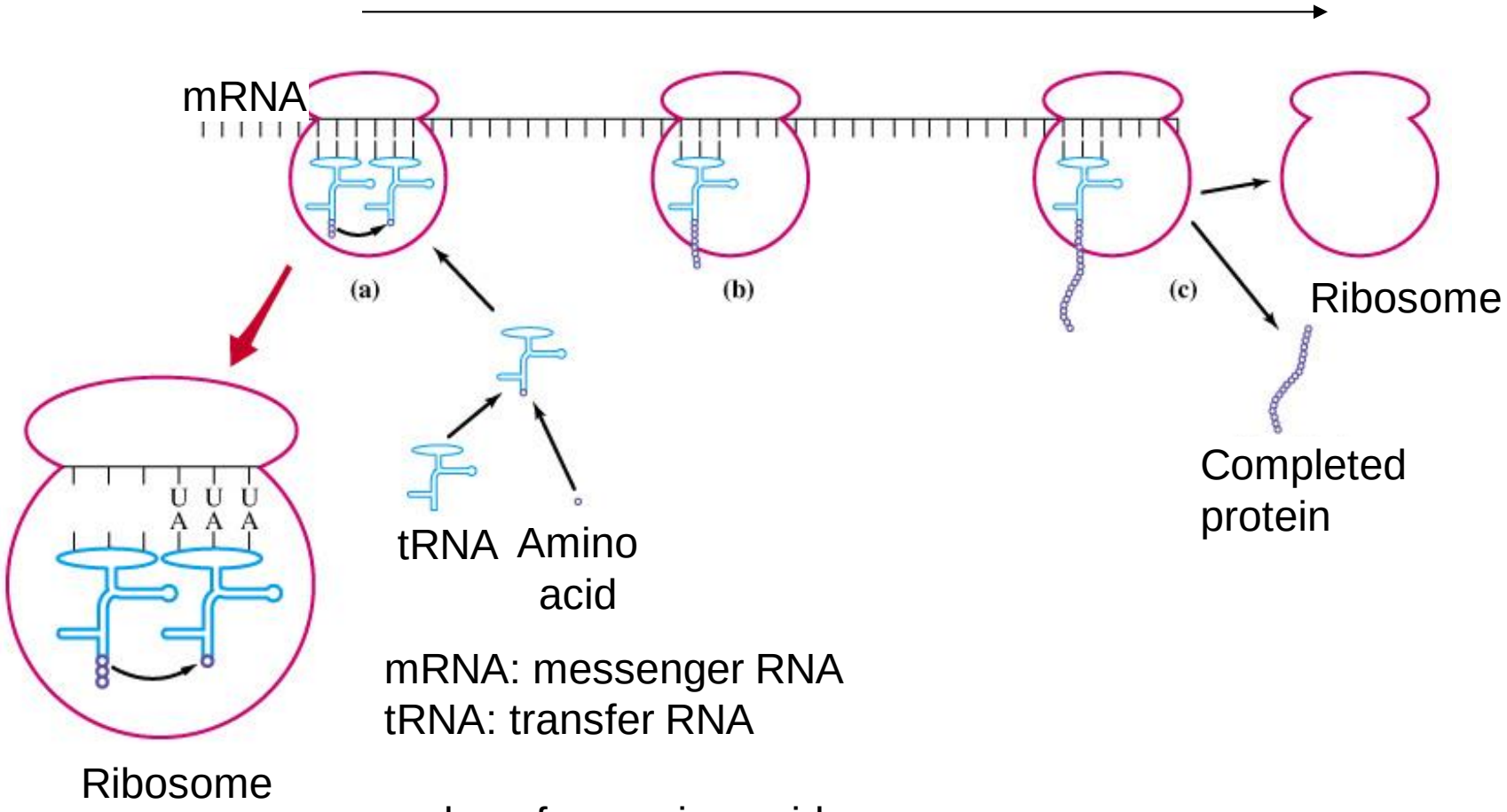
Alternatively: **copying of information to RNA** (single strand)

DNA: desoxy ribonucleic acid
RNA: ribonucleic acid

3. Self assembly and growth

Protein synthesis

Takes place in ribosome (organelle in the cell).



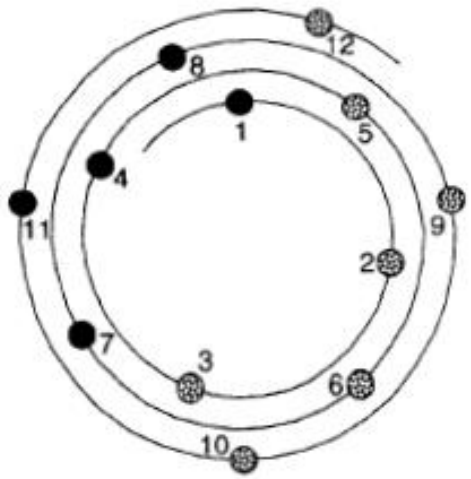
mRNA: messenger RNA
tRNA: transfer RNA

codon of an amino acid:
sequence of three nucleotides (eg. ACT, CAG, TTT)

3. Self assembly and growth

3.3 Examples of self-assembly in biology

3.3.1 Protein supercoils, e.g. alpha-Keratin



hydrophobic

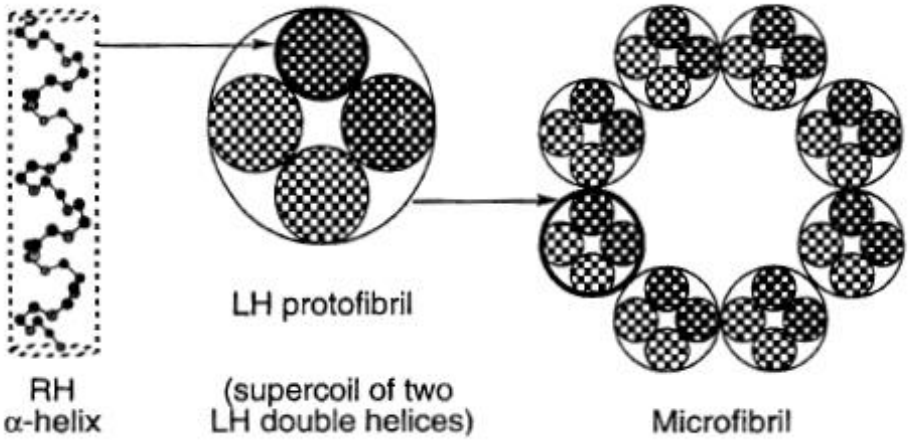
hydrophilic

The amino acids (some hydrophilic, some hydrophobic) are plotted in sequence around the spiral. α-helix involves 3.6 amino acids per turn, the angular separation of amino acids is 100°. This results in a hydrophobic stripe along one side of the helix.

From Elices, 2000. Chapter 8, E. Renuart and C. Viney

Hierarchical structure of a keratin microfibril. The representation of a molecular α-helix shows only the protein backbone for clarity.

From Elices, 2000. Chapter 8, E. Renuart and C. Viney.

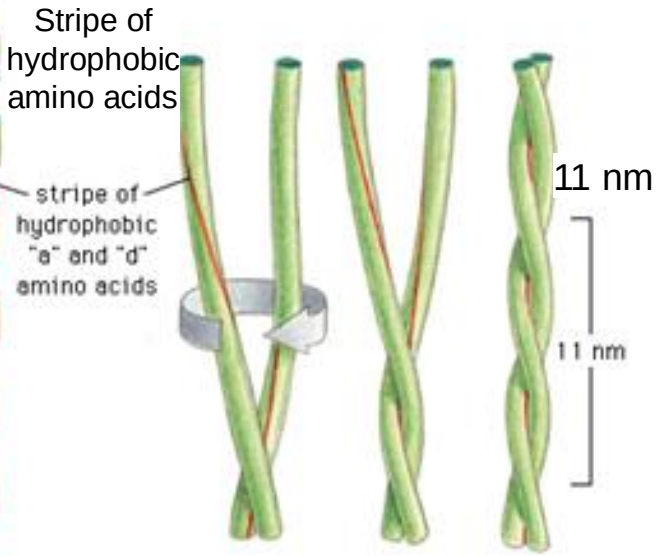


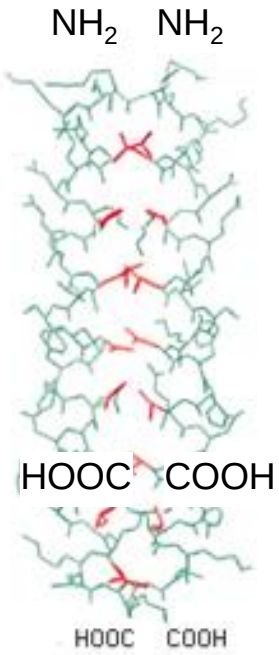
3. Self assembly and growth

Alpha keratin supercoil

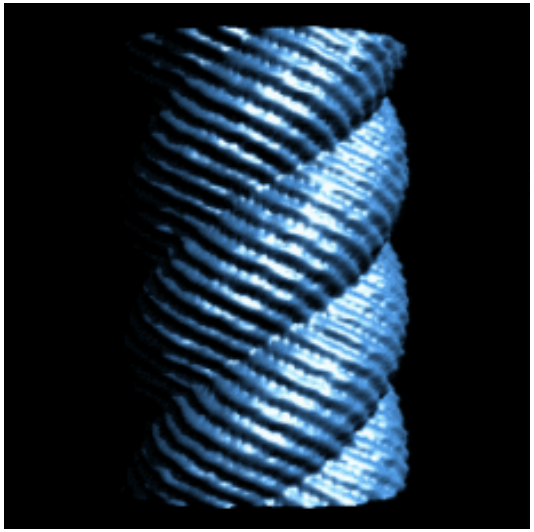
Keratin: 2 right-handed alpha helices combine to form left-handed superhelix.

Hydrophobic parts hidden in the interior of superhelix.





Technical example of supercoil:

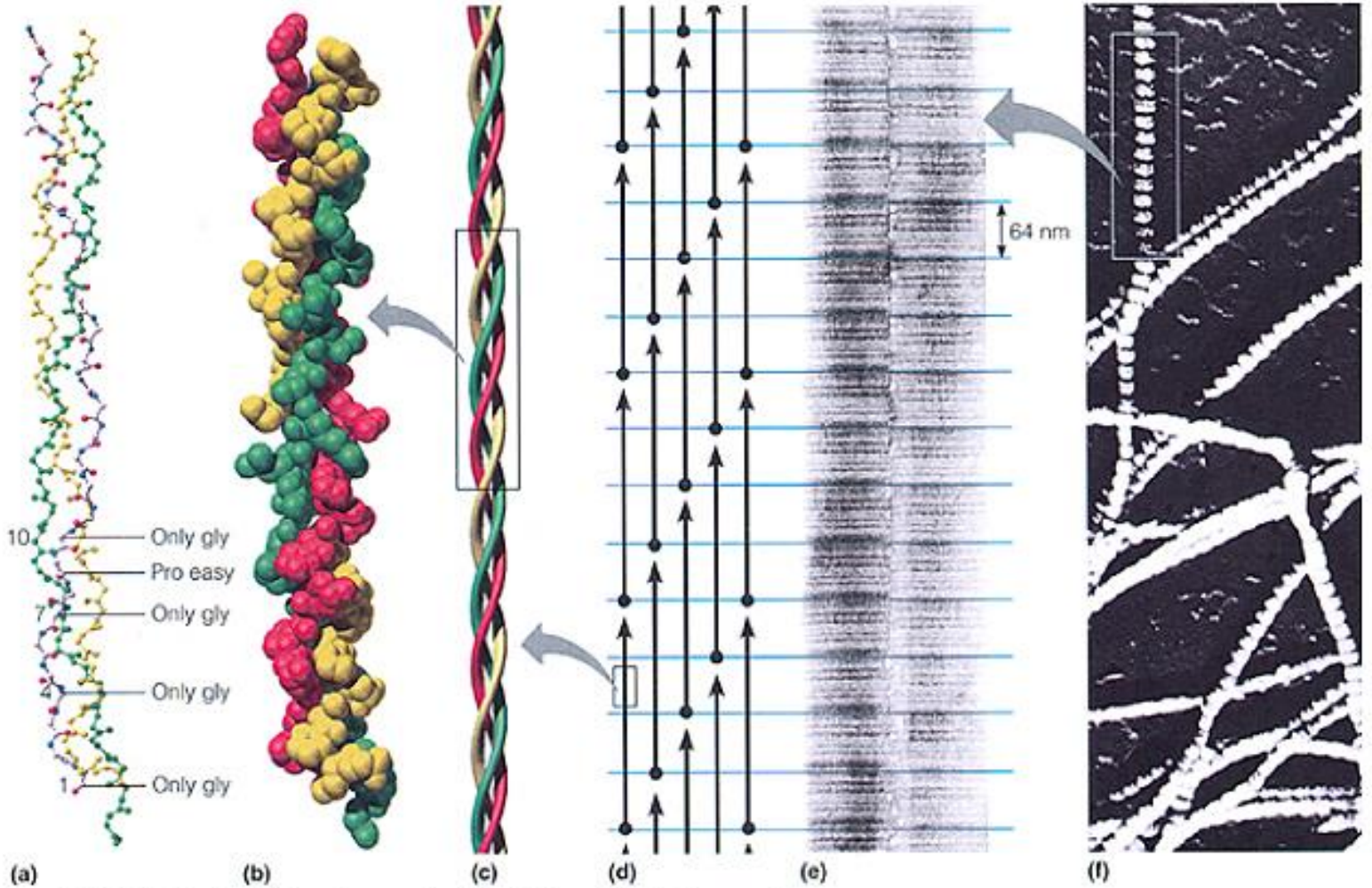


Rope

3. Self assembly and growth

More supercoils: Collagen

3 left-handed alpha-helices form one right handed superhelix

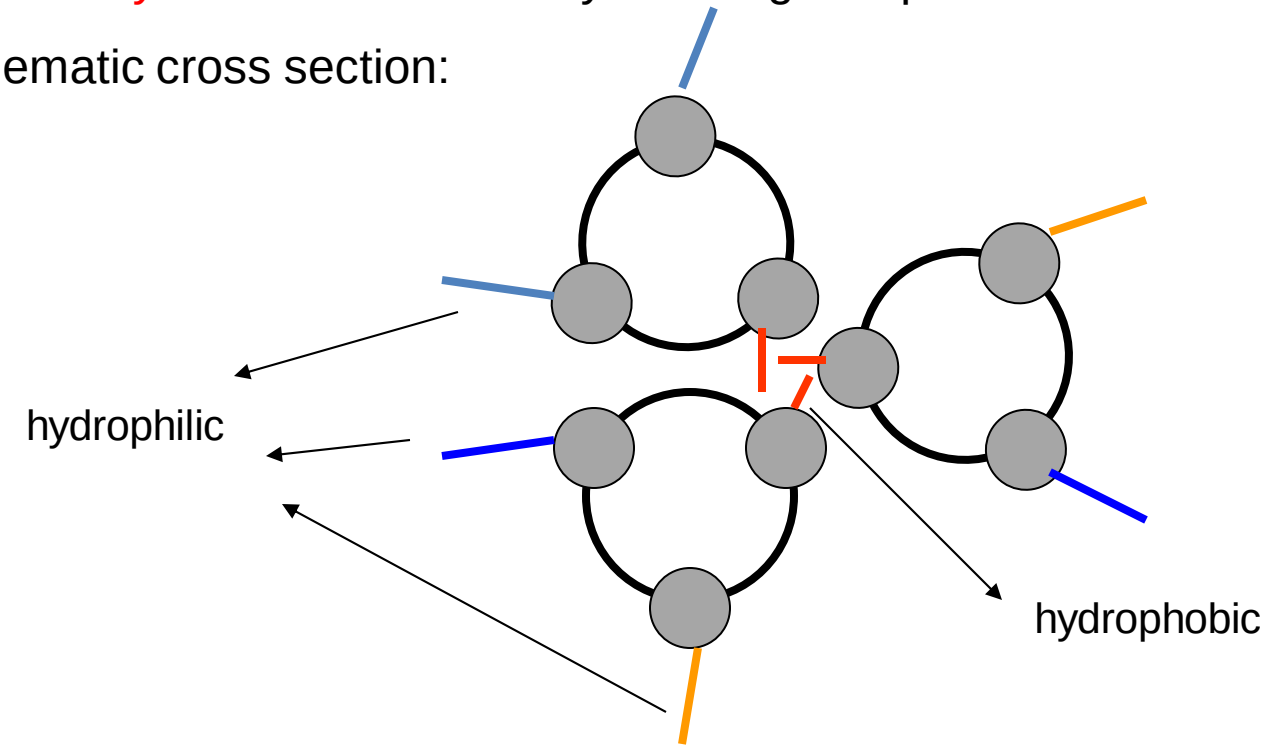


3. Self assembly and growth

Collagen triple helix

Role of Glycine in self-assembly of collagen triple helix.

Schematic cross section:



Residues: = Glycine: -H, = other residues

Glycine has smallest possible side group (H-atom) → 3 chains fit together.

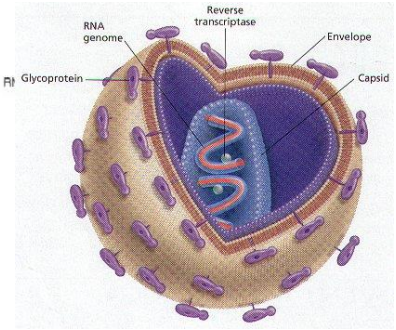
3. Self assembly and growth

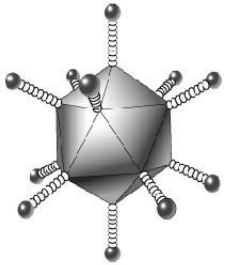
3.3.2 Viruses

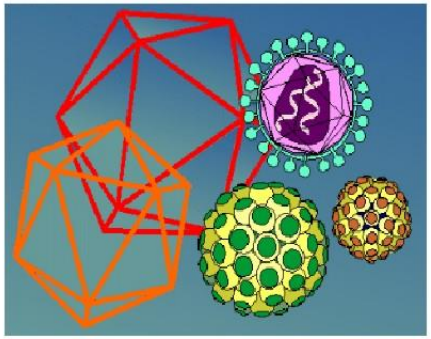
Viruses: (virus (latin) = slime, poison)

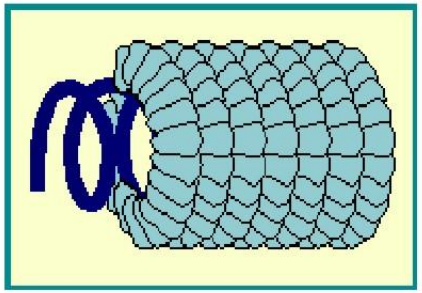
Discovered 1892 by D. J. Iwanowsky (tabac mosaic virus)

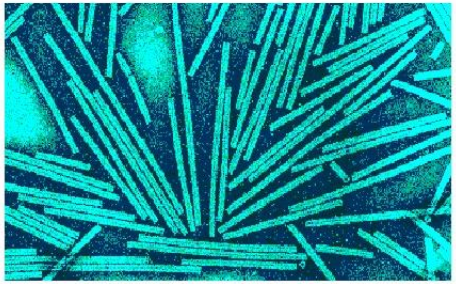
Viruses are nucleic acids with proteinaceous cover. Contain RNA or DNA.







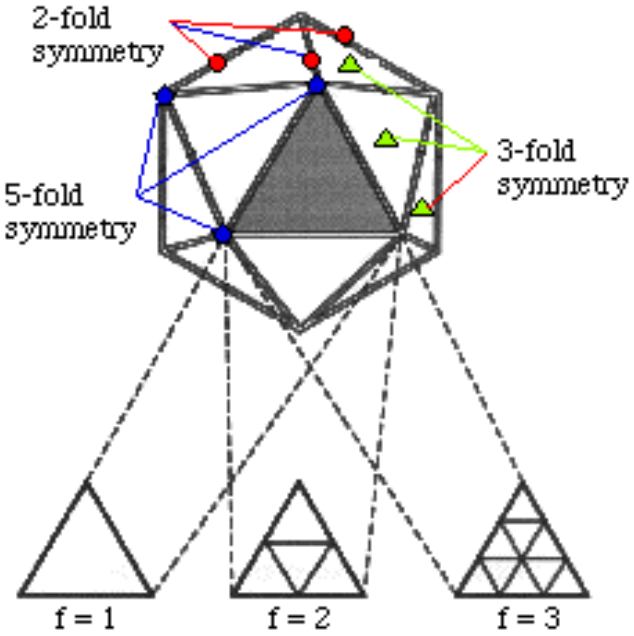




3. Self assembly and growth

Geometry consideration for virus capsids

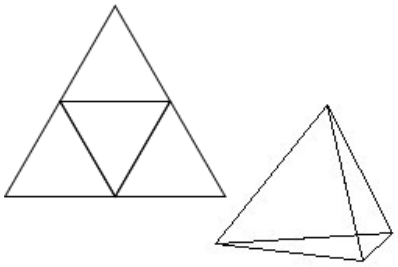
Self-assembly of icosahedral (20 sided polyhedron) viral capsid



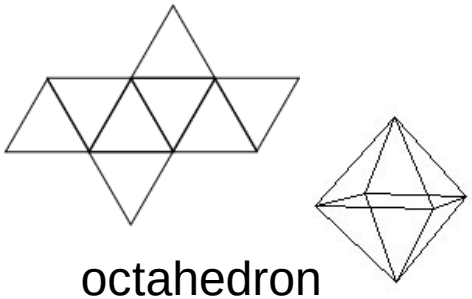
Icosahedric virus capsids are found in adenovirus, reovirus, many plant viruses, herpes virus.

3. Self assembly and growth

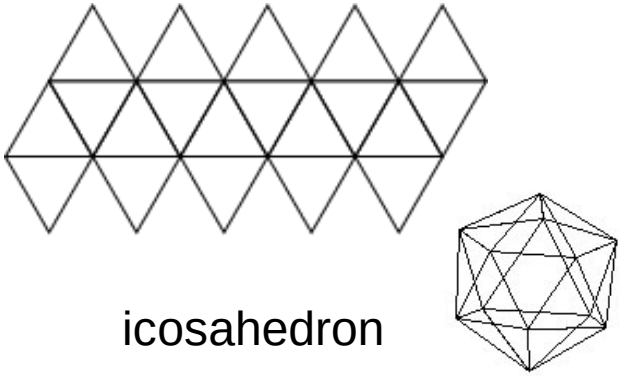
Construction of a closed shape from identical polyhedra



tetrahedron



octahedron



icosahedron

	n = 3 triangles S E V	n = 4 squares S E V	n = 5 pentagons S E V	n = 6 hexagons S E V
r = 3	4 6 4 tetrahedron	6 12 8 cube	12 30 20 dodecahedron	∞ 2D-lattice
r = 4	8 12 6 octahedron	∞ 2D-lattice		
r = 5	20 30 12 icosahedron			
r = 6	∞ 2D-lattice			

S: number of sides

E: number of edges

V: number of vertices

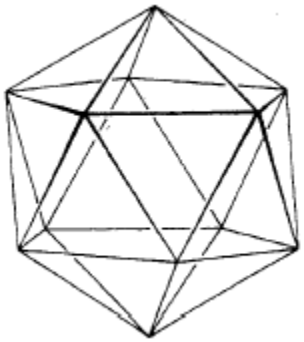
n: number of edges per element

r: number of edges that meet in one vertex

r = 2 E/V (because each edge has two end points)

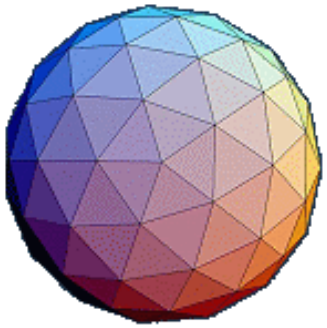
3. Self assembly and growth

Spherical viruses

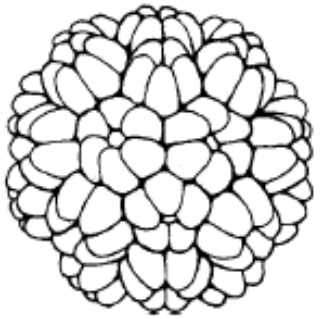


Icosahedron

Truncated icosahedron



Geodesic dome

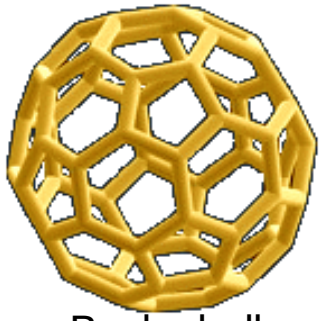


virus

FIGURE 4.15. *Geodesic domes are derivatives of icosahedrons, figures with twenty triangular faces and twelve points at which five edges converge. The dome in the middle divides each face into nine smaller triangles (notice the five-strutted junctions retained from the original icosahedron). A viral shell of equivalent form (such as the cowpea chlorotic mottle virus on the right) has 180 protein molecules; the old icosahedral apexes are replaced by rings of five and the old faces by rings of six.*

Other representations of geodesic domes:

Soccer ball



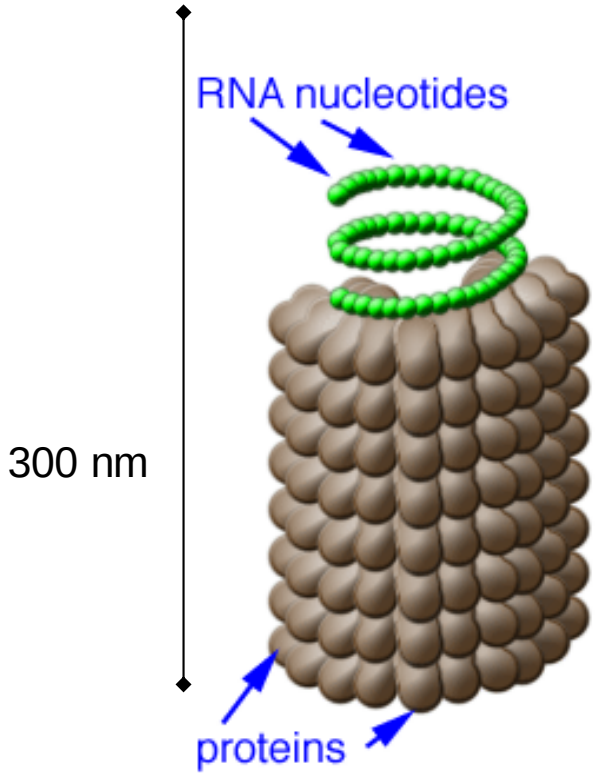
Bucky-ball: C_{60} molecule

3. Self assembly and growth

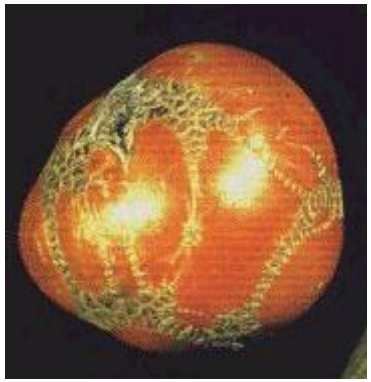
Tabacco mosaic virus

Plant virus that infests tabacco and related plants (e.g. tomato). First virus to be self-assembled in the laboratory.

Rod-like virus consists of tube shaped protein capsid and RNA strand inside:



tabacco



tomato

3. Self assembly and growth

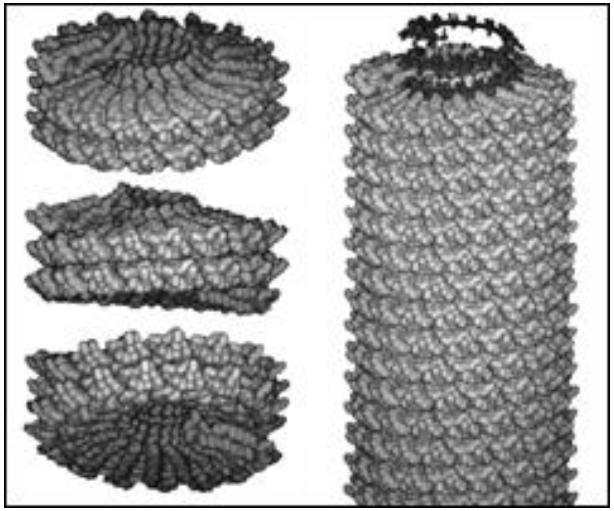
Self Assembly of tabacco mosaic virus

First performed by by H.L. Fraenkel-Conrat und R.C. Williams in 1955.

TMV capsid and RNA was separated into components (6400 nucleic acids und 2130 identical protein units).

Purified components placed in solution → after 24 h re-assembly into functional viruses!

Schematic of TMV capsid assembly:



Process in vivo is much faster! (Interaction of RNA and protein)

3. Self assembly and growth

Summary self assembly and growth

Self assembly of identical parts reduces info needed for construction plan

Self assembly is governed by ‚weak' interactions:
van der Waals, electrostatic, hydrophilic-hydrophobic

LCs (liquid crystals) are an extremely common motif in self-assembled materials (not only biological ones). They consist of elongated units that assemble into (quasi)ordered structures.
Examples: liquid crystalline display (LCD), spider silk

Proteins:
primary structure is coded for (AA sequence), secondary+tertiary structure by self-assembly:
- keratin: double helix
- collagen triple helix
  (stabilized by hydrophilic-hydrophobic interactions)

Special examples of self assembly of larger structures:
viral capsids (icosahedral virus, tabacco mosaic virus)

4. Mechanical concepts in biomaterials

Concepts of specific importance in biomaterials

- Elasticity / viscoelasticity
- **Hydration** dependence
- **Composite** materials
- Optimization of **fracture toughness**
- High efficiency by **microstructure**
- **Light weight** (cellular)

:

4. Mechanical concepts in biomaterials

Chemical bonds and mechanical properties

Type of bonding influences mechanical behavior:

Bonding type	***Material***	***Optimized Property***
Covalent & strongly directional: • aligned chains • extensive cross-linking	silk horn	tensile stiffness (1D) compressive stiffness (3D)
Non covalent & weakly directional • hydrogen bonds • hydrophobic bonds	cellulosics viral spikes	wet strength rigidity in aqueous environment

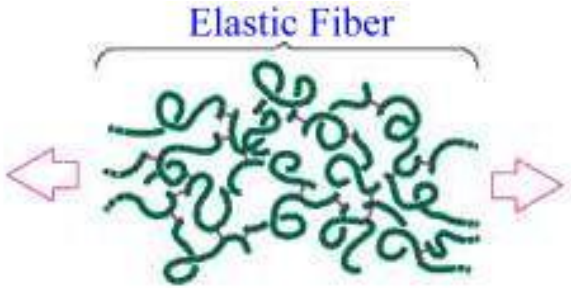
4. Mechanical concepts in biomaterials

4.1 Rubber elasticity

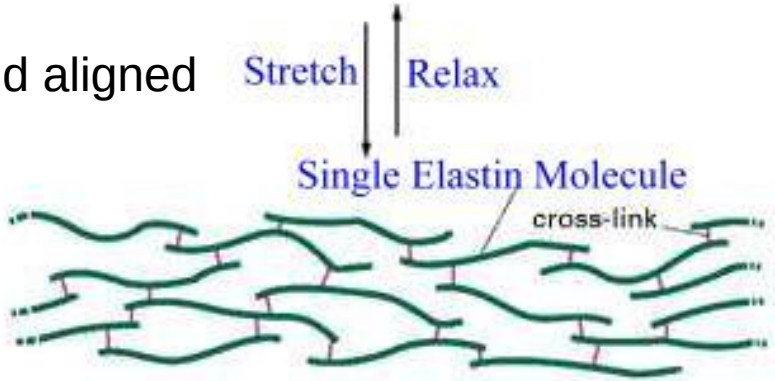
Rubber elasticity is a rare behavior in biological materials. Occurs in protein rubber.

Principle of rubber elasticity: based on entropy

Curled up fibers, high entropy



Get stretched and aligned lower entropy



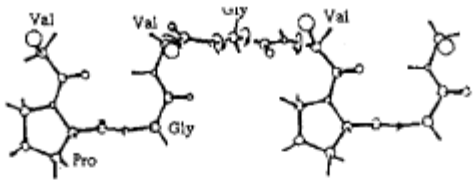
Snap back into curled up state, to achieve state of high entropy again!

latex: rubbery properties only upon vulcanization

Degree of cross-linking in soft rubbers approx. 1%

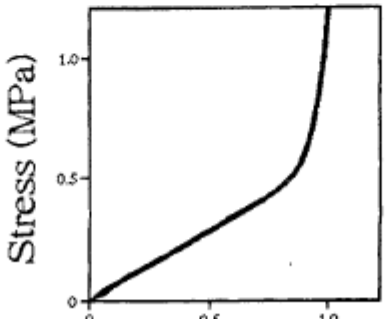
4. Mechanical concepts in biomaterials

Elastin



β-turn of elastin, showing the rotations which lead to the elastic properties (Urry 1983). *From J. Vincent, 1990.*

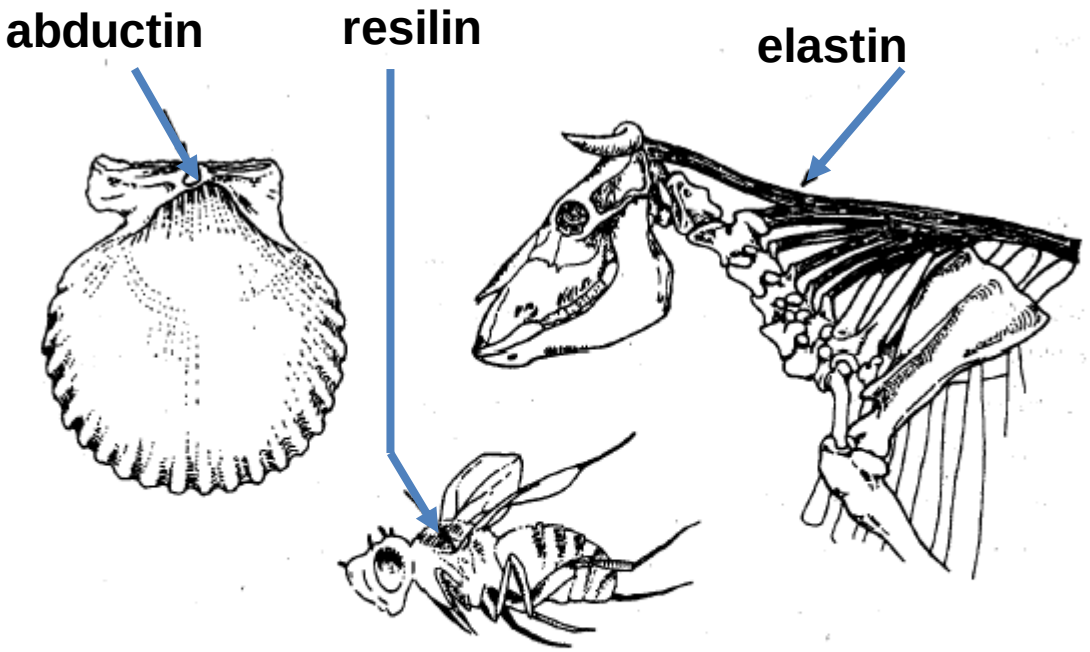
Assembly of β-turns into the primary elastin helix which is further assembled into fibers (Urry 1983). *From J. Vincent, 1990.*



Stress-strain curve for ligamentum nuchae (Dimery *et al.* 1985). *From J. Vincent, 1990.*

4. Mechanical concepts in biomaterials

Types of protein rubbers



Three different elastic proteins, characteristic of three different organisms.

Abductin (in sea shells): The scallop uses abductin in the hinge of the shell

Resilin (in insects): the fly has a pad of resilin in the hinge of each wing

Elastin (in vertebrates): the ligament connecting the head and thoracic vertebrae of a cow is largely elastin. Elastin also in artery walls, skin, elastic cartilage. Usually associated with collagen. *From S. Vogel, 1998.*

4. Mechanical concepts in biomaterials

Resilin

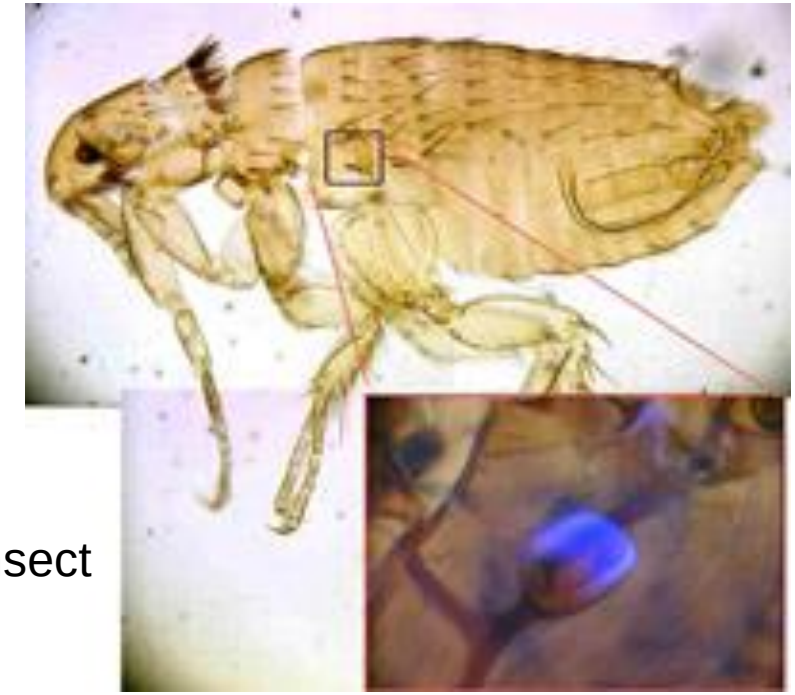
Protein rubber in insects.

Very high resilience (“elastic efficiency): 96-97 % (i.e. almost all elastic energy can be recovered after deformation). Equivalent to best synthetic rubbers.

Makes wing movement more efficient, muscle power only in one direction.

Examples:

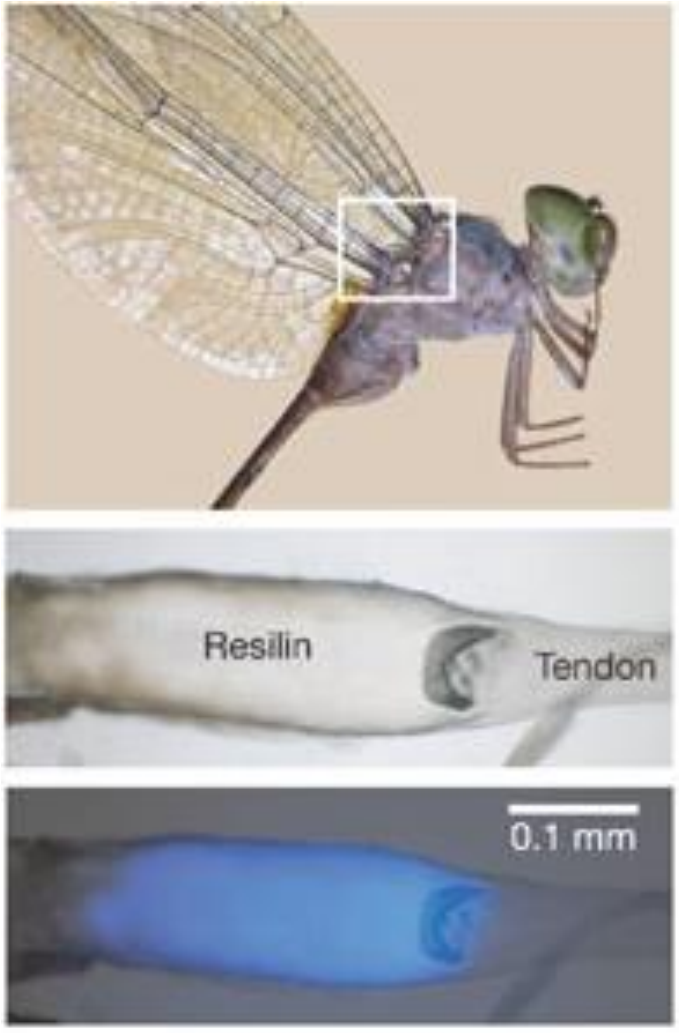
Resilin in hinge of wing of flying insect



Resilin pad in flea

4. Mechanical concepts in biomaterials

Resilin in dragonfly wing tendon



Fluorescence of resilin in the wing tendon from adult dragonfly (*Zyxomma* sp.).

The lower panels show photomicrographs of the tendon in phosphate-buffered saline under white light and ultraviolet light.

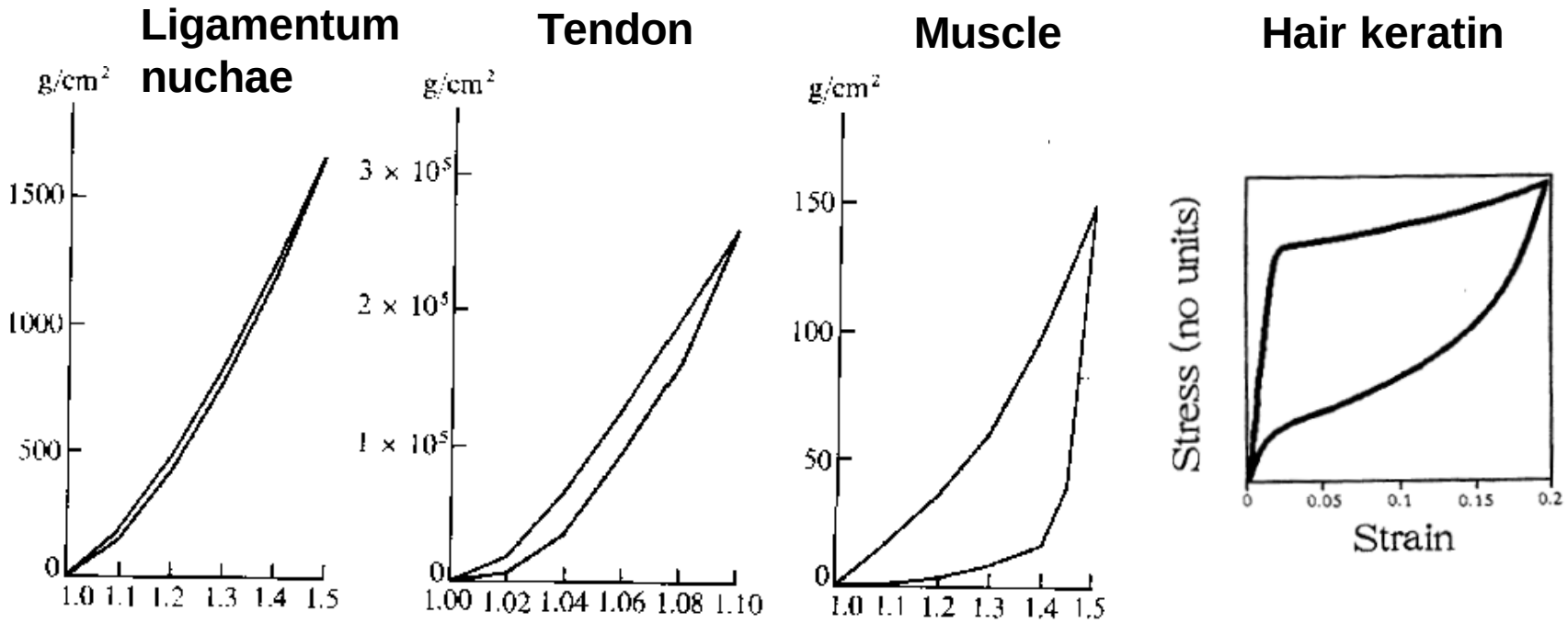
C.M. Elvin, et al. (2005). Synthesis and properties of crosslinked recombinant pro-resilin. *Nature* **437** (7051), 999-1002.

4. Mechanical concepts in biomaterials

4.2 Viscoelasticity

Normal behavior in biological materials. Deformation can be described as combination of elastic deformation and viscous flow.

Materials show hysteresis.



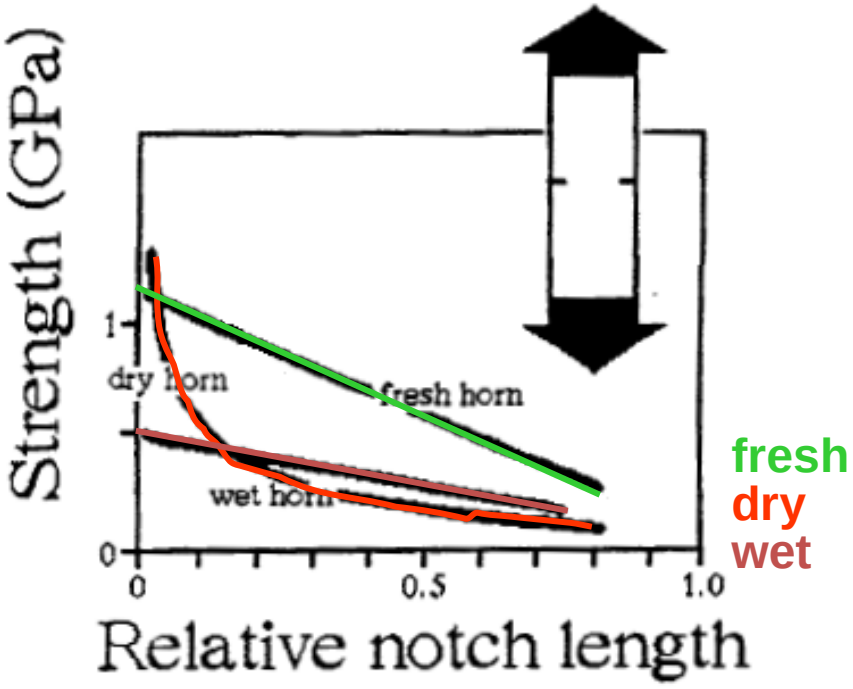
Patterns of hysteresis loop in non-vascular tissues. The abscissas show the stretch ratio; the ordinates, stress (Azuma and Hasegawa, 1973).

4. Mechanical concepts in biomaterials

4.3 Hydraton dependence

Most biological materials show different behavior when wet (physiological condition) or when dry.

Example: horn keratin



Notch sensitivity of horn keratin (Kitchener 1988), adapted from Fig. 5.15 J. Vincent 1990

4. Mechanical concepts in biomaterials

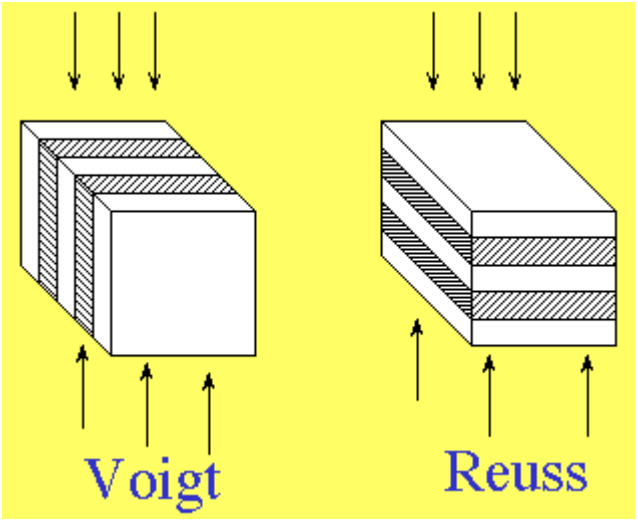
4.4 Composite materials

Most biological materials consist of more than one material phase (composite structure.

Stiffness of composite:

Highly dependent on orientation of composite components with respect to applied force.

$$E_c = E_f V_f + E_m (1 - V_f)$$



$$\frac{1}{E_c} = \frac{V_f}{E_f} + \frac{1 - V_f}{E_m}$$

E_c: Young's modulus (elastic modulus, stiffness) of composite

E_f, E_m: Young's moduli of stiff phase ("fiber") and soft phase ("matrix")

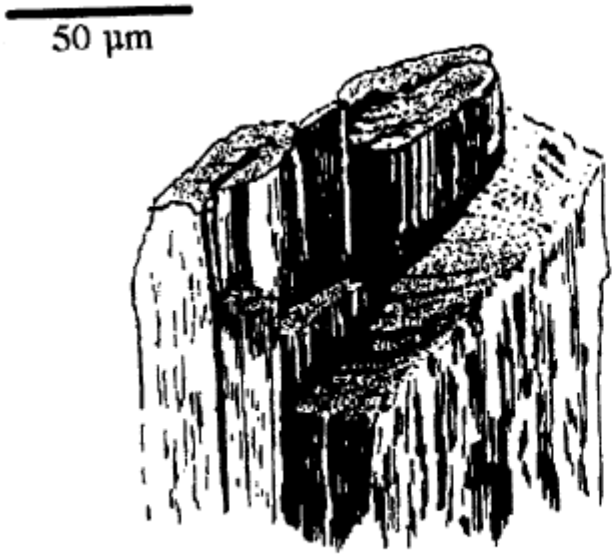
V_f: Volume fraction of stiff phase, 1-V_f: volume fraction of matrix

4. Mechanical concepts in biomaterials

Arrangement of fibers in composites

Examples: chitinous fiber composite tissue in insects, fractured in tension

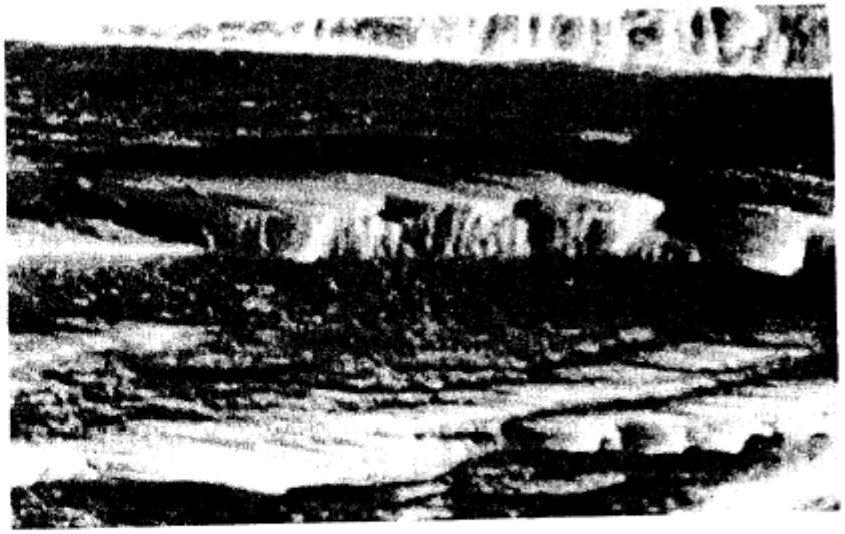
Locust tendon



Broken end of locust tendon. Relatively smooth fracture surface (brittle fracture). Crack partly deflected vertically.

Stiffness: E=11 GPa longitudinal, E=0.15 GPa transverse

Insect cuticle



Typical fracture produced from a cuticle with layers. Complex fracture surface, high fracture energy (high toughness).

Stiffness: E= 4 GPa

4. Mechanical concepts in biomaterials

4.5 Fracture toughness

Strategies to increase fracture toughness

1. The strain energy is unable to reach the crack tip: strain energy dissipated by plastic yield and failure of the material remote from crack; viscous effects can slow down the rate of delivery of energy to the crack tip (crack can be porpagated only slowly)

example: transfer of fluid from one site to another within the material (probably a mechanism for toughening teeth)

2. The total energy for cracking is raised: large fracture surface or the material at the crack tip may deform plastically

3. The stress at the crack tip is de-focused by increasing its radius of curvature (the sharpness of the crack tip governs the stress intensity)

4. Dissipation of energy by fiber extension or pull-out

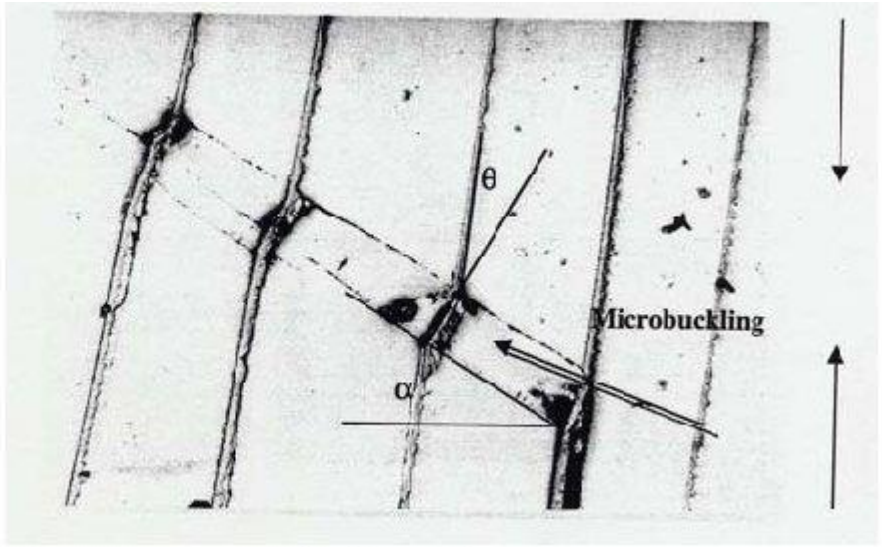
5. Prestressing of material in opposite sense: e.g. in compression if the most likely loads will be tensile, so the prestress has to by paid off first

6. The entire structure is so small that the strain energy cannot be stored

4. Mechanical concepts in biomaterials

Ad 1) Failure remote from the crack

Example: Microbuckling of mineral platelets in mother of pearl (abalone shell nacre) in compressive testing:



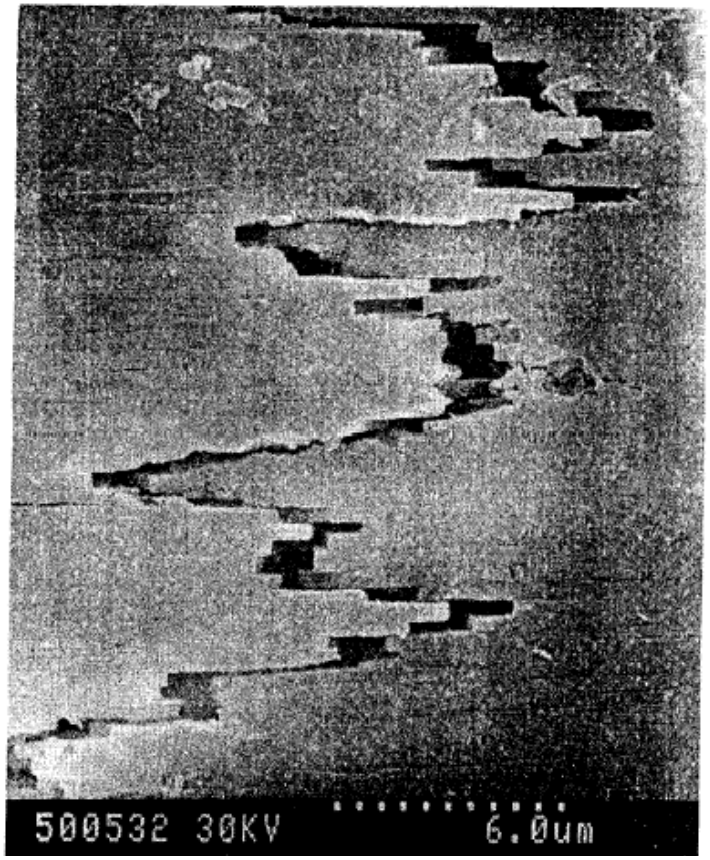
Strain energy is dissipated by failure of the material far away from the crack

4. Mechanical concepts in biomaterials

Ad 2) Large fracture surface

Example: fracture path in nacre (mother of pearl).

Complicated fracture path generates large fracture area, requires large fracture energy.

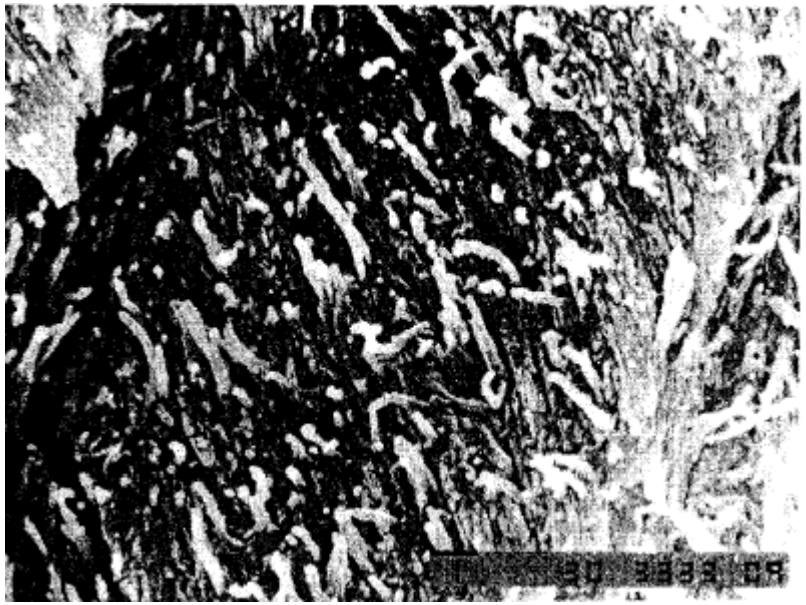


From J. Vincent, 1990.

4. Mechanical concepts in biomaterials

Ad 4) Fiber pull-out

Pulling out of fibers requires large amount of energy, integrity of structure preserved over a wide range of load.



Fracture surface of antler, showing separation of collagen and mineral fibers

4. Mechanical concepts in biomaterials

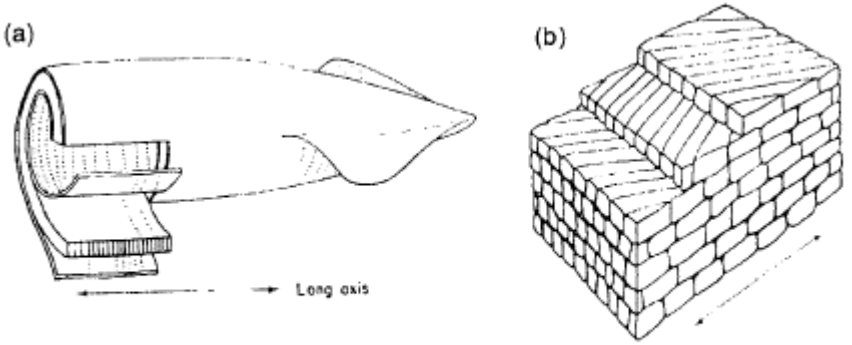
Ad 5) Pre-stressing

Pre-stressing of the structure in opposite sense, e.g. in compression - if material is expected to be loaded in tension. Or fibrous cell walls may be pre-stressed in tension be inner pressure, to avoid fiber buckling upon compression.

Example: plant cells

Parenchyma cells in potato.

Example: tissue of tunicates, arrangement of fibers in the tunicae.

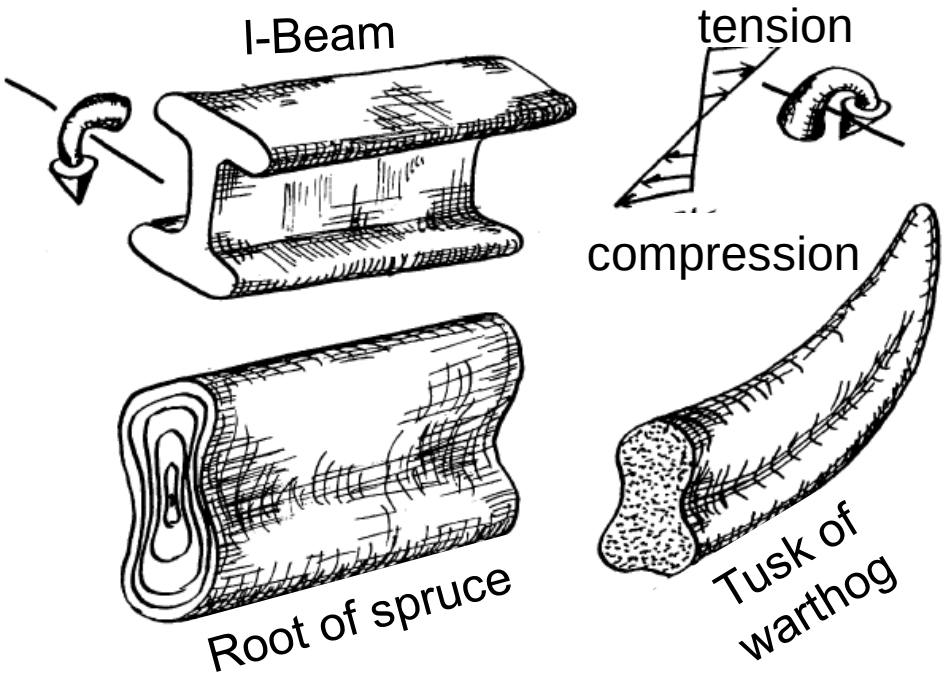


4. Mechanical concepts in biomaterials

4.6 Efficiency of structures

Natural and technical structures may be optimized on the macroscopic scale to resist a specific loading pattern and use as little material as possible.

Example: I-beam structures in bending



They are wider (more material) where higher bending stresses (tension or pressure) act on them, and narrower (less material) where there are lower stresses. *From Mattheck and Kubler, 1995.*

4. Mechanical concepts in biomaterials

Efficient choice of material

„Efficiency of a structure“: ratio between load carried P and weight of the structure itself P/W

P/W depends on:

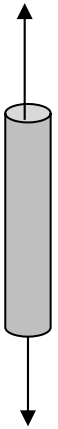
- material efficiency
- contribution from loads and geometry of the structure

Comparison between different materials can be made in relation to the function that they have to perform!

4. Mechanical concepts in biomaterials

Stiffness controlled structures

Stiffness controlled tensile structure (fiber):



$$\frac{P}{W} \propto \frac{E}{\rho} \cdot \frac{n^{1/2}}{l\, n^{1/2} + k\, P^{1/2} \sigma^{-1/2}}$$

Materials efficiency criterion

Structural loading coefficient

E: Young‘s modulus, σ: tensile strength

ρ: density

n: number of elements acting in parallel to carry load

l: distance over which the load is carried, k: constant

P: load carried by the structure

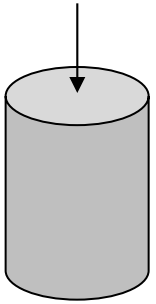
W: weight of the structure itself

From: Elices (2000), Pergamon Materials Series, Chapter 2

4. Mechanical concepts in biomaterials

Stiffness controlled compressive structure (column):

Criterion for column that should not buckle under its own (+ external) load, e.g. trees



$$\frac{P}{W} \propto \frac{E^{1/2}}{\rho} \cdot \frac{P_{crit}^{1/2}}{l^2 \, n^{1/2}}$$

Materials efficiency criterion

Structural loading coefficient

E: Young's modulus, σ: tensile strength

ρ: density

n: number of elements acting in parallel to carry load

l: distance over which the load is carried, k: constant

P: load carried by the structure, P_{crit}: critical load for buckling under compression

W: weight of the structure itself

4. Mechanical concepts in biomaterials

Stiffness controlled compressive structure (panel):

Criterion for optimized panel to limit deflection

$$\frac{P}{W} \propto \frac{E^{1/3}}{\rho} \cdot \frac{P_{crit}^{\ 2/3}}{l^{5/3}\, n^{2/3}}$$

Materials efficiency criterion

Structural loading coefficient

E: Young‘s modulus, σ: tensile strength

ρ: density

n: number of elements acting in parallel to carry load

l: distance over which the load is carried, k: constant

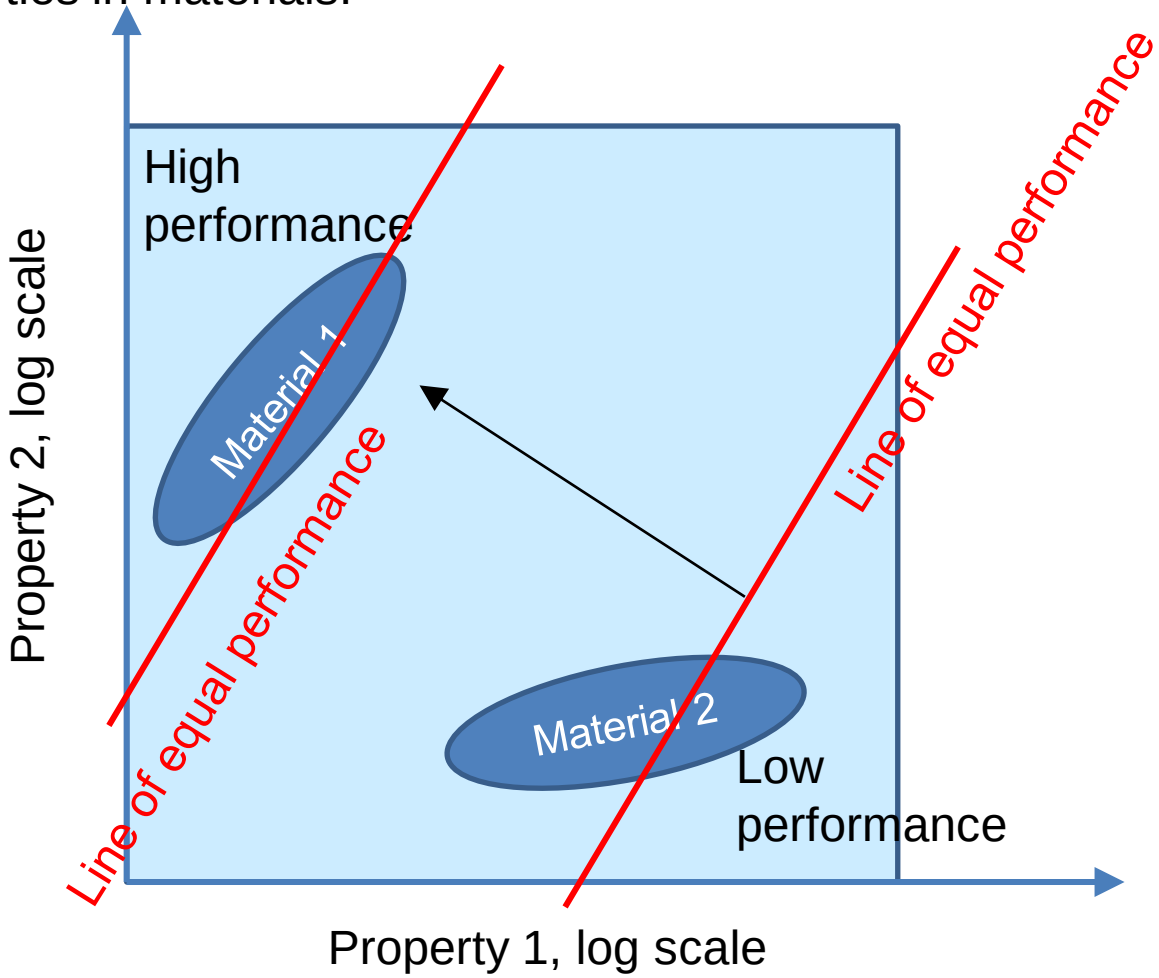
P: load carried by the structure, P_{crit}: critical load for buckling under compression

W: weight of the structure itself

4. Mechanical concepts in biomaterials

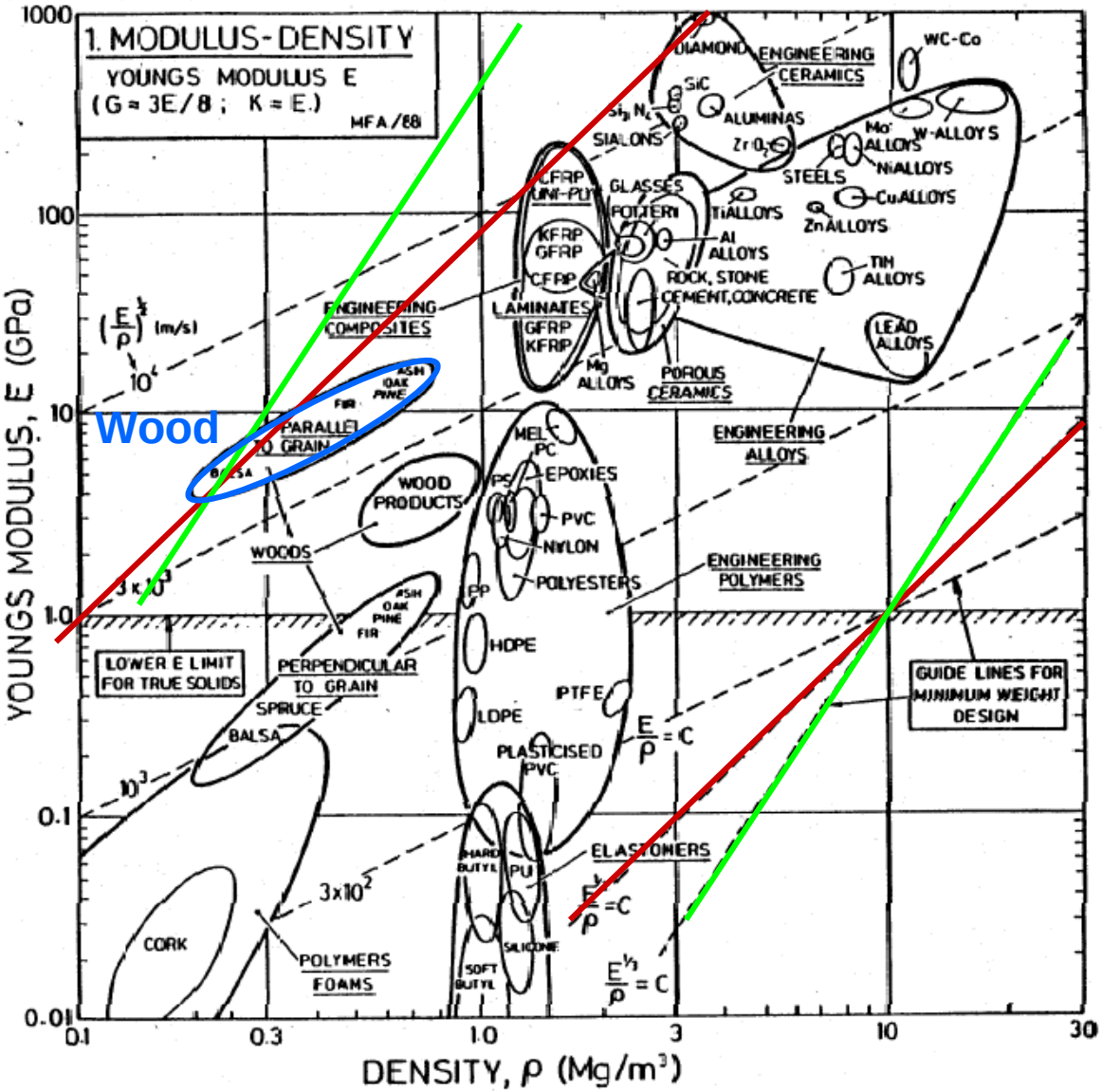
Ashby plot

Also Ashby map, developed by M.F. Ashby. Used to visualize performance related ratio of properties in materials.



4. Mechanical concepts in biomaterials

Ashby plot: stiffness - density



$P/W \propto E/\rho^2$

column loaded in compression, resist buckling

$P/W \propto E/\rho^3$

beam, minimize bending

4. Mechanical concepts in biomaterials

Stiffness – density table

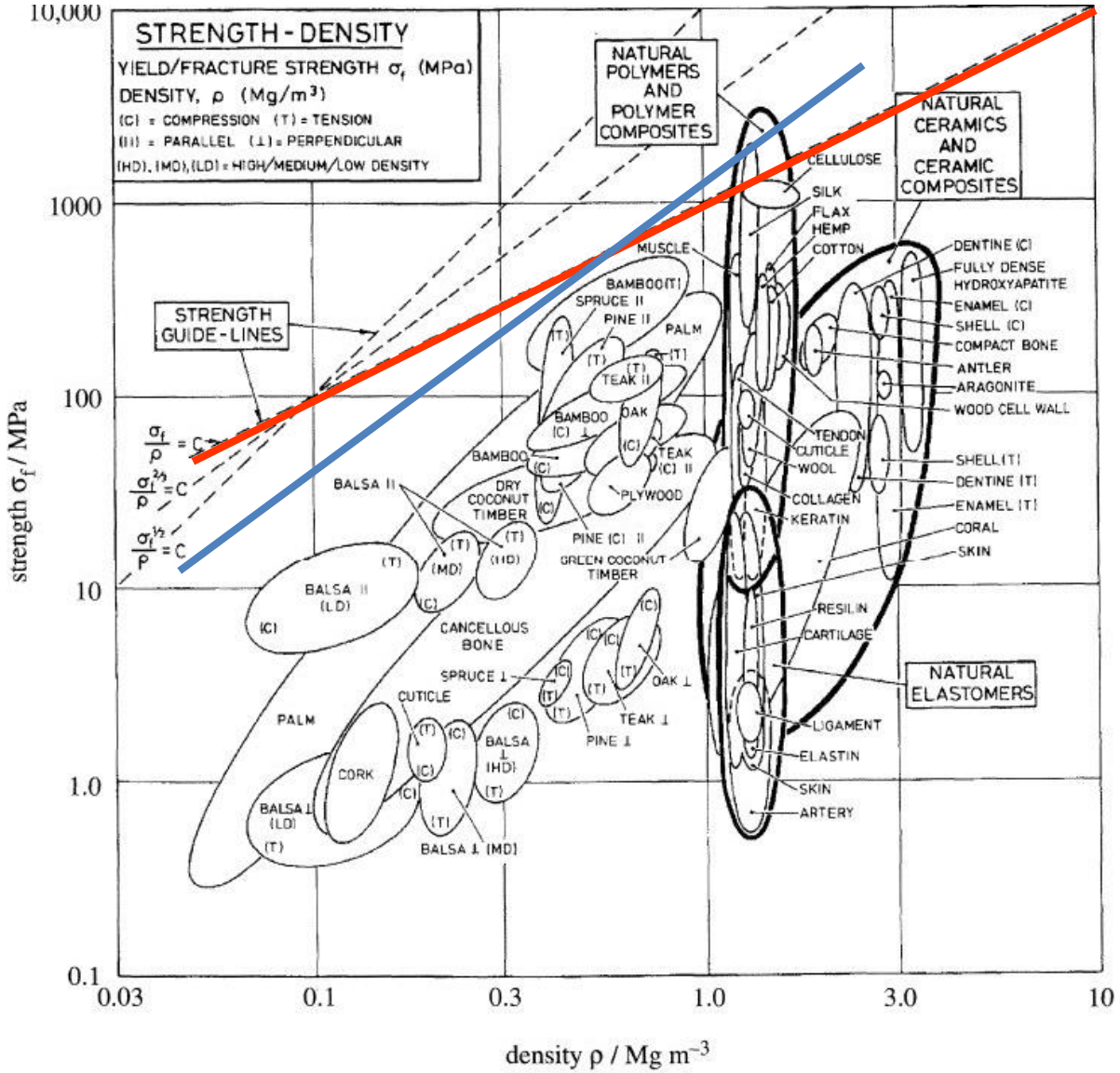
tension compression bending

material	E [a]	ρ [b]	$M_1 = E/\rho$ [c]	$M_2 = E^{1/2}/\rho$ [d]	$M_3 = E^{1/3}/\rho$ [e]
single cellulose fibre	100.0	1.5	67	6.7	(3.1)
wood cell wall	35.0	1.5	23	3.9	(2.2)
balsa (HD)	5.5	0.3	18	7.8	(5.9)
balsa (MD)	4.0	0.2	20	10.0	(7.9)
balsa (LD)	2.0	0.1	20	14.1	(2.9)
oak	11.5	0.7	16	4.8	(3.2)
pine	11.0	0.5	21	6.3	(4.2)
spruce	9.0	0.4	21	7.1	(5.0)
teak	12.0	0.65	18	5.3	(3.5)
bamboo (bulk material)	22.5	0.75	30	6.3	(3.8)
palm (*Iriartea*)	3.5	0.15	23	12.5	(10.1)
palm (*Welfia*)	11.0	0.55	20	6.0	(4.0)
coconut timber	7.0	0.5	14	5.3	(3.8)
plywood	8.0	0.6	13	4.7	3.3
single carbon fibre	390.0	2.0	195	9.9	(3.6)
CFRP unidirectional	200.0	1.5	133	9.4	(3.9)
CFRP laminate	50.0	1.5	33	4.7	2.5
mild steel	210.0	7.9	27	1.8	(0.8)

Units: [a]GPa, [b]Mg m^{-3}, [c]GPa (Mg m^{-3})$^{-1}$, [d]GPa$^{1/2}$ (Mg m^{-3})$^{-1}$, [e]GPa$^{1/3}$ (Mg m^{-3})$^{-1}$.

4. Mechanical concepts in biomaterials

Ashby plot: strength - density



Tensile and compression load $\frac{\sigma_f}{\rho}$

Bending load $\frac{\sigma_f^{2/3}}{\rho}$

4. Mechanical concepts in biomaterials

Strength – density table

			tension	compression	bending
material	σ_f [a]	ρ [b]	$M_4 = \sigma_f/\rho$ [c]	$M_5 = \sigma_f^{2/3}/\rho$ [d]	$M_6 = \sigma_f^{1/2}/\rho$ [e]
single cellulose fibre	1000	1.5	667	66.7	(21.1)
single cotton fibre	350	1.5	233	33.1	(12.5)
single flax fibre	250	1.5	167	26.5	(10.5)
single hemp fibre	400	1.5	267	36.2	(13.3)
single silk fibre	2000	1.3	1500	120.0	(35.0)
single wool fibre	100	1.3	77	16.6	(7.7)
balsa (HD)	24	0.3	80	27.7	(16.3)
balsa (MD)	20	0.2	100	36.8	(22.4)
balsa (LD)	16	0.1	160	63.5	(40.0)
pine	160	0.7	229	42.1	(18.1)
oak	180	0.53	340	60.2	(25.3)
spruce	240	0.42	571	92.0	(36.9)
teak	150	0.65	231	43.4	(18.8)
bamboo (bulk material)	400	0.75	533	72.4	(26.7)
coconut timber	45	0.5	90	25.3	(13.4)
palm	100	0.42	240	50.0	(24.0)
plywood	35	0.6	58	17.8	9.9
single carbon fibre	2200	2.0	1100	84.6	(23.5)
CFRP unidirectional	1200	1.5	800	75.3	(23.1)
CFRP laminate	600	1.5	400	47.4	16.3
mild steel	400	7.9	51	6.9	2.5

Units: [a]MPa, [b]Mg m^{-3}, [c]MPa (Mg m^{-3})$^{-1}$, [d]MPa$^{2/3}$ (Mg m^{-3})$^{-1}$, [e]MPa$^{1/2}$ (Mg m^{-3}).

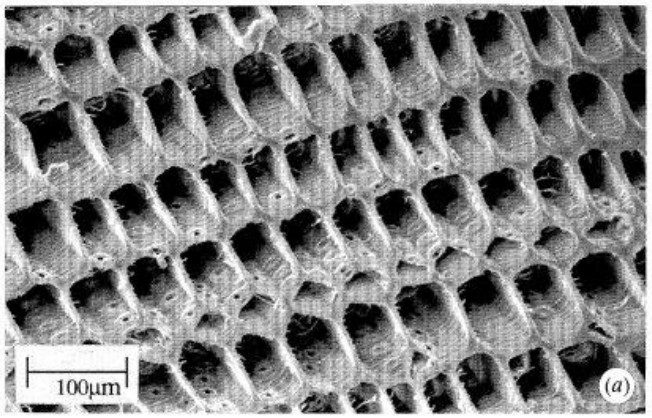
4. Mechanical concepts in biomaterials

Efficiency by microstructure

Cellular materials

Many biological materials achieve good mechanical performance at very low weight by cellular structure.

Example: wood



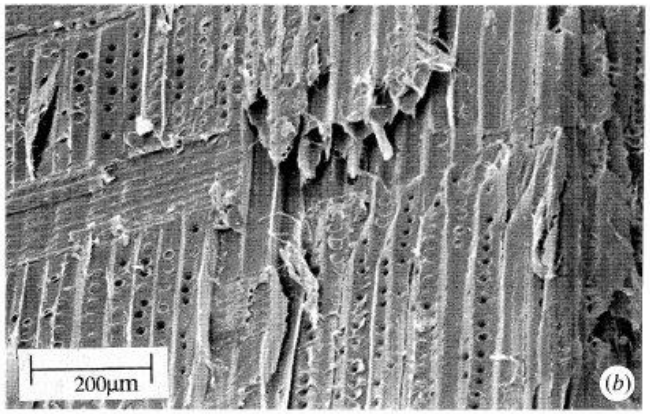
(a)

Scanning electron micrographs of Norway spruce (Picea abies):

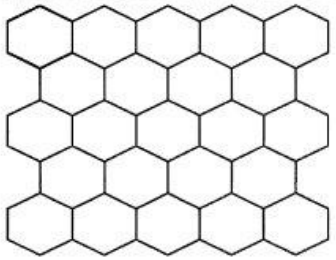
(a) cross section and

(b) longitudinal section;

(c) schematic of wood structure, idealizing as a honeycomb-like array of hexagonal cells.



(b)



(c)

4. Mechanical concepts in biomaterials

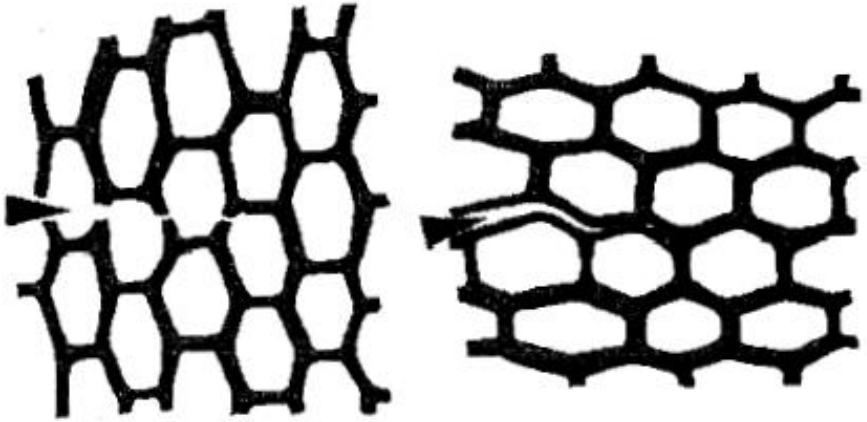
Fracture of wood

Influence of cellular structure on fracture behavior

Wood cells in longitudinal direction

Fracture of wood cells in tension (G. Jeronimidis). *From J. Vincent, 1990.*

Wood cells in cross section



Direction difficult to split

Direction easier to split

Tangential or radial?

4. Mechanical concepts in biomaterials

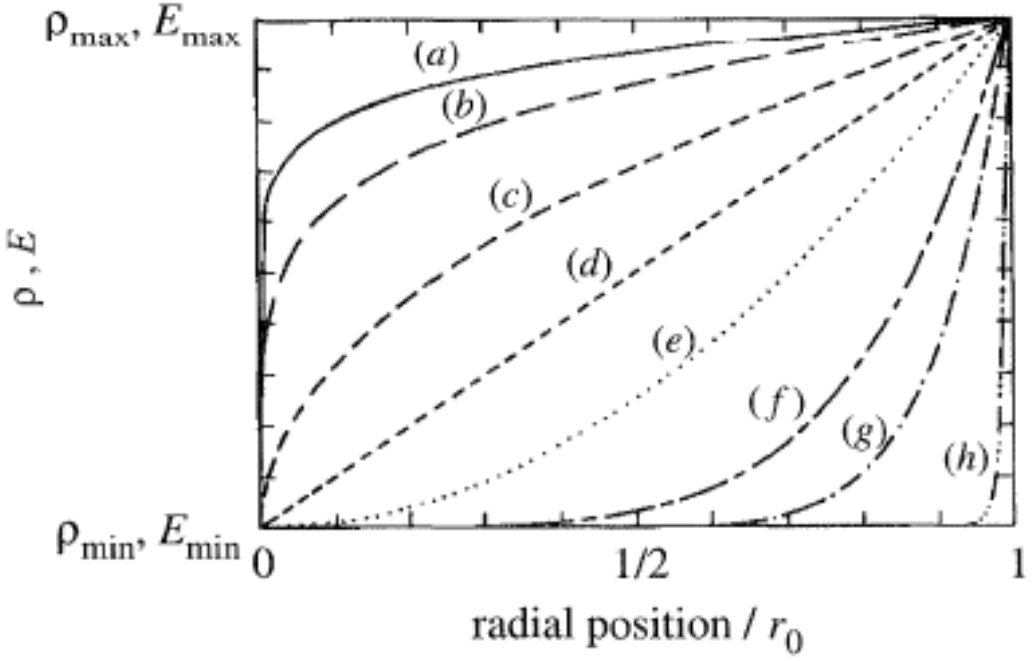
Density gradients and flexural stiffness

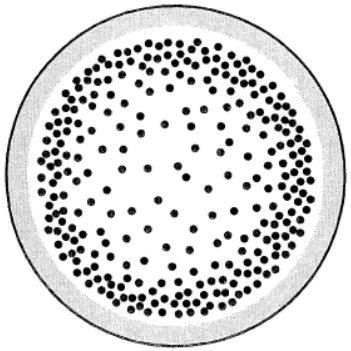
Consider theoretical rod-like structure with density varying radially from ρ_{min} at the center to ρ_{max} at the periphery according to

$$(\rho - \rho_{min})/(\rho_{max} - \rho_{min}) = (r/r_o)^n ;$$

by varying the volume fraction of pores.

The dependence of the radial variation in density or Young's modulus on the parameter n: n= (a) 0.1, (b) 0.2, (c) 0.5, (d) 1, (e) 2, (f) 5, (g) 10, (h) 100.





density gradient:
$\rho(r)=\rho_{min}+(r/r_0)^n (\rho_{max}-\rho_{min})$

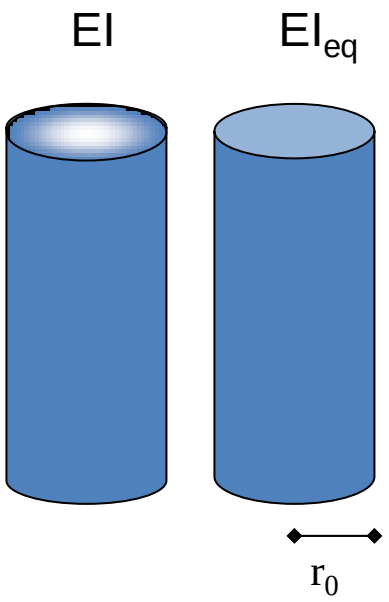
4. Mechanical concepts in biomaterials

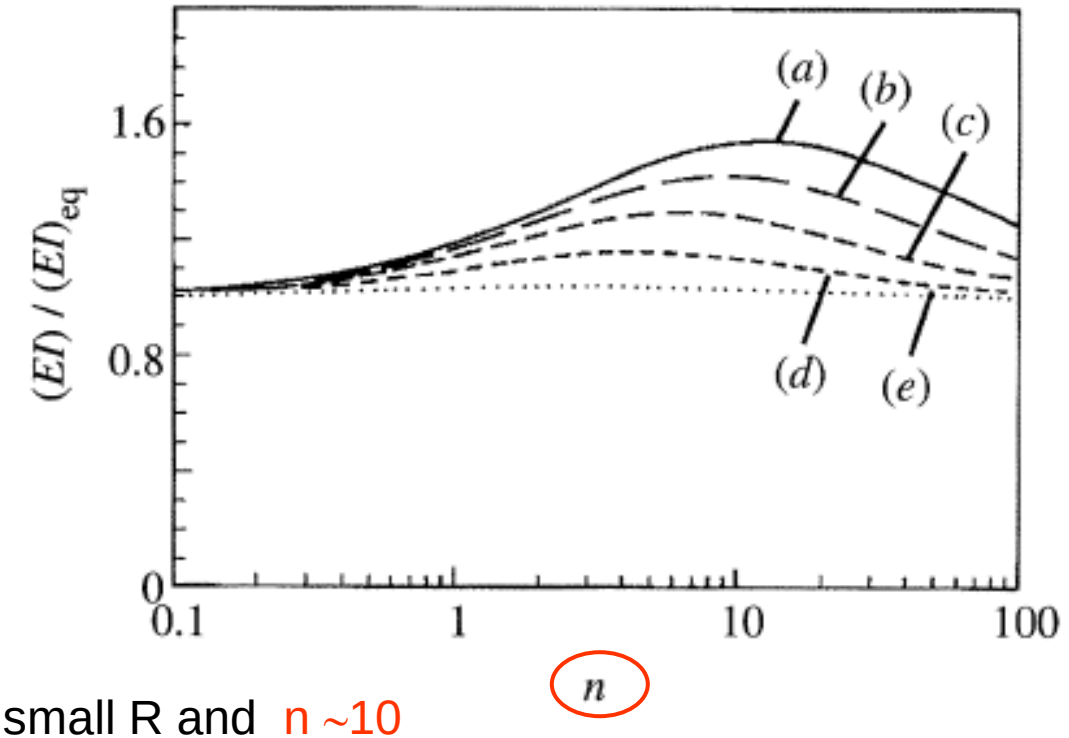
Density gradients and flexural stiffness

The flexural rigidity of a composite beam with a radial density gradient normalized by that of a solid circular cross-section of equal mass, EI/EI_{eq} .

Density ratio $R=\rho_{min}/\rho_{max,}$ R = (a) 0.05, (b) 0.1, (c) 0.2, (d) 0.4, (e) 0.8

Density gradient: $\rho(r)=\rho_{min}+(r/r_0)^n(\rho_{max}-\rho_{min})$



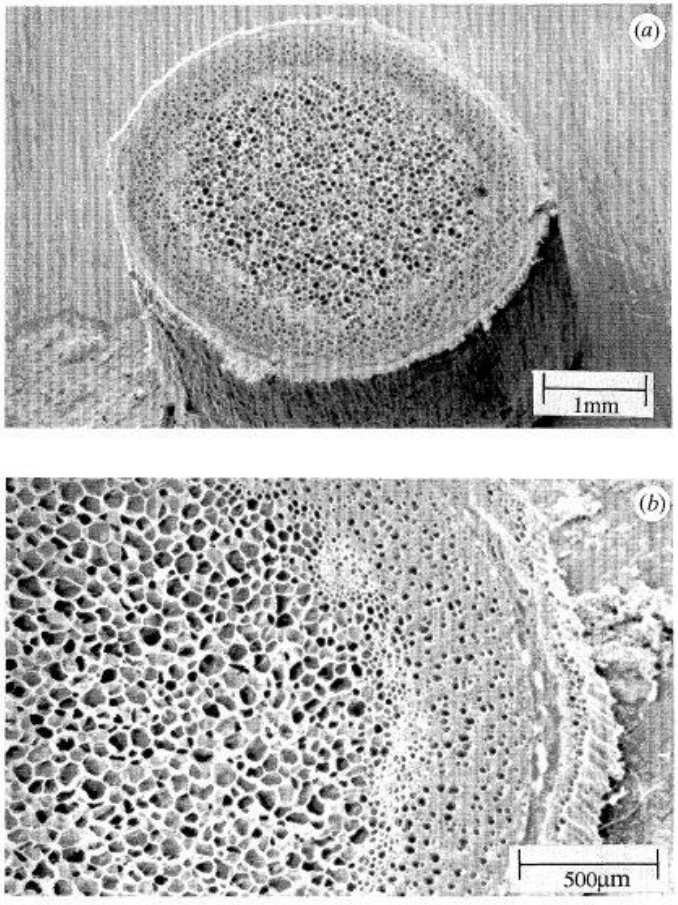


Maximum of EI/EI_{eq} at small R and n ~10

4. Mechanical concepts in biomaterials

Density gradients in nature

e.g. plant stems

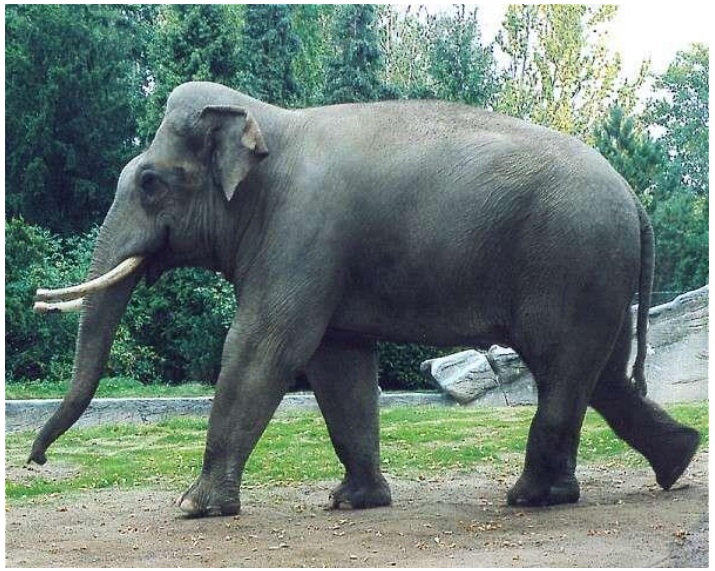


Scanning electron micrograph of hawthorn (Crataegus) showing the outer, almost fully dense, cylindrical shell with an inner layer of foam-like parenchyma cells.

4. Mechanical concepts in biomaterials

4.7 The issue of scaling

Small or large structures have different shapes!



4. Mechanical concepts in biomaterials

Summary mechanical concepts

Rubber elasticity in biology: elastin, resilin, abductin are exceptions!!
most biomaterials are highly viscoelastic (e.g. hair keratin)

Mechanical properties are *not constant*: change with hydration
(material may become weaker *or* stronger upon addition of water);

Main issues:

fracture toughness
- composite materials
- fiber pull-out
- crack deviation
- etc. etc.

efficiency
- light weight structures (economic use of material, cellular materials, optimized shapes)
- optimization through microstructure

5. Soft tissues: skin, cartilage, glue

Mechanical properties of “soft” tissues

Table of some representative organs mainly consisting of soft connective tissue:

Material	Ultimate tensile strength [Mpa]	Ultimate tensile strain [%]	Collagen (% dry weight)	Elastin (% dry weight)
Tendon	50-100	10-15	75-85	< 3
Ligament	50-100	10-15	70-80	10-15
Aorta	0.3-0.8	50-100	25-35	40-50
Skin	1-20	30-70	60-80	5-10
Articular Cartilage	9-40	60-120	40-70	-

Compare with harder and stiffer biological materials:

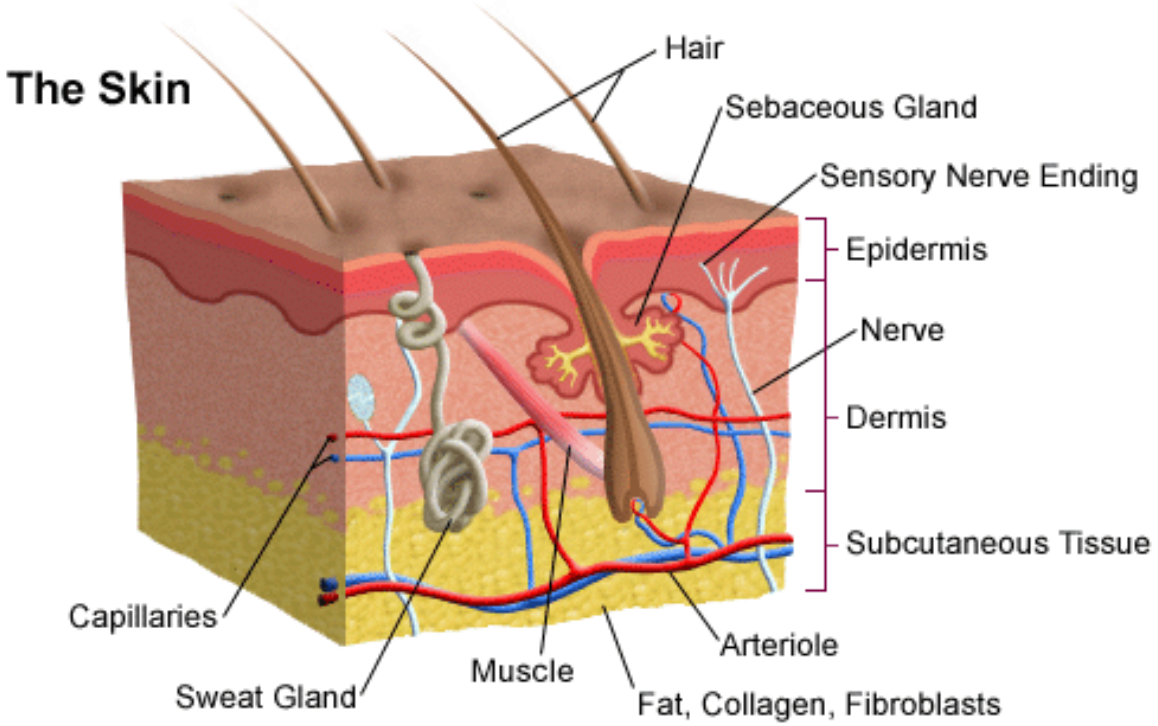
bone: UTS=130 MPa

wood cell wall: UTS=1GPa

5. Soft tissues: skin, cartilage, glue

5.1 Skin

Layered structure:



Epidermis: outermost layer, carries surface structures such as hair, feathers, or scales.

Dermis, or corium layer of skin: consists of connective tissue fibers (primarily collagen fibers)

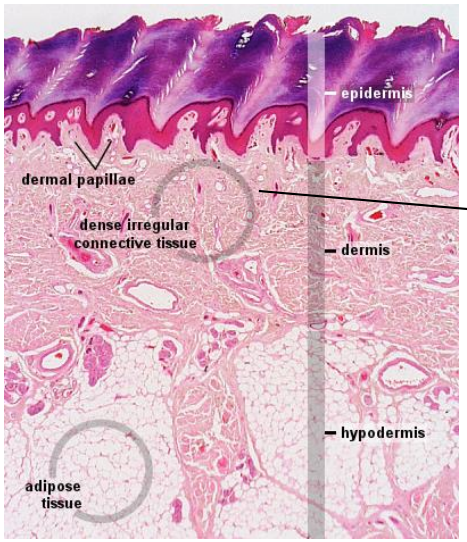
Hypodermis (subcutaneous tissue): looser connective tissue

5. Soft tissues: skin, cartilage, glue

Dermis

Dense fiber network of collagen, load carrying layer, subjected to mixed loading modes (tension, torsion, shear, compression).

collagen associated with elastin (large extension at low applied stress)



DERMIS, rich in collagen

Leathermaking:

Relies on dermis, the epidermis generally is removed (except with furs).

Tanning chemically fixes the ionizable side groups of the collagen fibrils by increasing hydrogen bonding between collagen molecules.

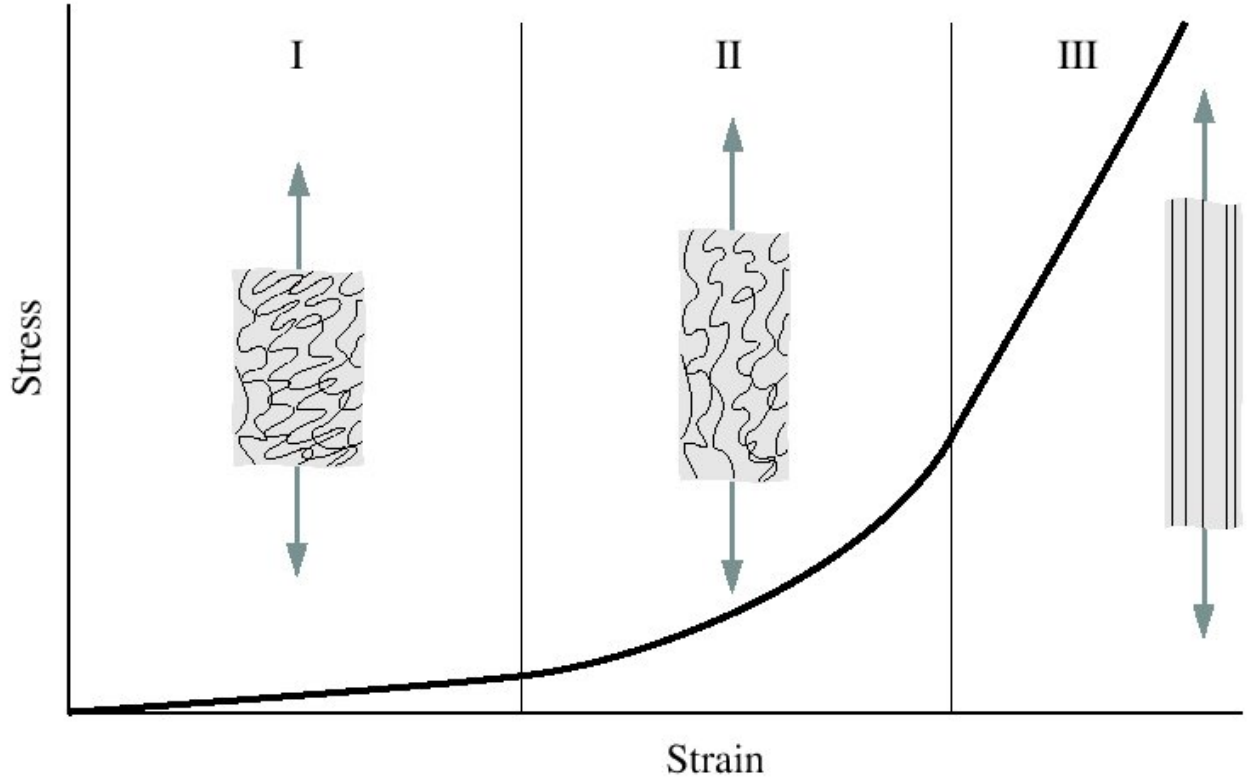
5. Soft tissues: skin, cartilage, glue

Mechanical properties of skin

Typical behavior of skin in tension:

I and II: kinked fibers get stretched

III: stiffening, pulling on stretched molecules

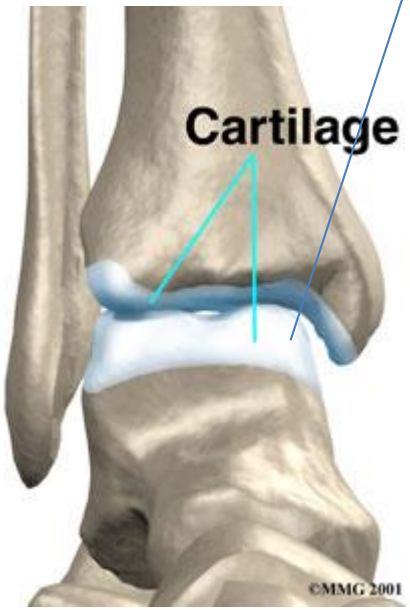


High work of fracture (high toughness)

5. Soft tissues: skin, cartilage, glue

5.2 Cartilage

Types of cartilage



Hyaline cartilage

- Small, evenly distributed collagen fibers (50 - 80 % dry weight)
- Negligible elastin content
- Glassy smooth appearance
- Examples: Articular cartilage, growth plate, rib/costal cartilage , support of trachea (wind pipe), nasal septum

Fibrous cartilage

- More numerous, densely packed collagen fibers than hyaline cartilage (about 90% dry weight)
- Examples: Outer portion of intervertebral disc (annulus fibrosus), meniscus of knee (padding, shock absorption)

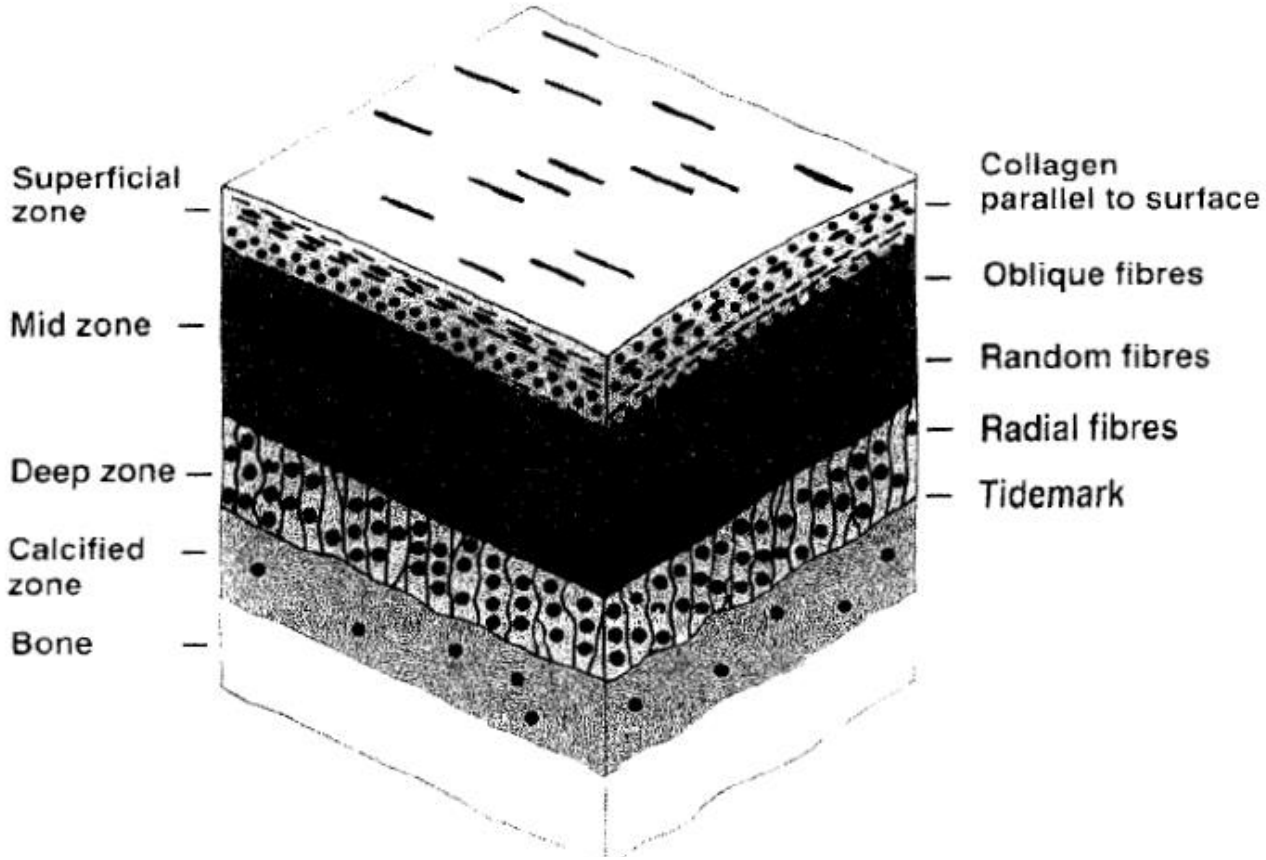
Elastic cartilage

- Similar to hyaline cartilage, but also contains elastin fibers - therefore more flexible
- Present in structures subject to repeated bending
- Examples: external auditory canal, eustachian tube

5. Soft tissues: skin, cartilage, glue

Structure of cartilage

Natural cartilage shows complex layered structure with collagen fibers in specific orientation in each of the layers.



Structural variation through the thickness of articular cartilage showing zonal arrangement of chondrocytes and collagen fibers. *From Elices, 2000.*

5. Soft tissues: skin, cartilage, glue

Composition of cartilage

Table: Relative proportion of non-cellular components in adult human articular cartilage.

	wet weight
Collagen	15-20%
Proteoglycan	3-15%
Water	65-80%
Non-collagenous proteins and glycoproteins*	1%

*e.g. cartilage oligomeric matrix protein (COMP), fibronectin, anchorin.

Proteoglycans: huge molecules consisting of protein and sugar -> proteoglycans

Proteoglycan network:

1. Hyaluronan (hyaluronic acid)

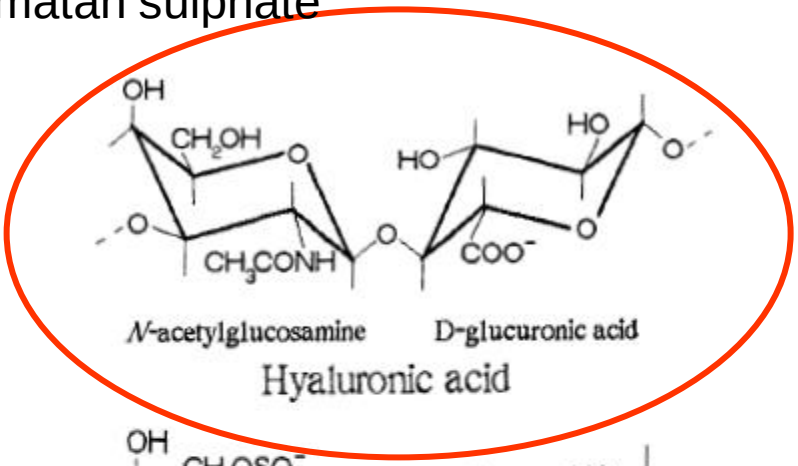
2. Aggrecan

5. Soft tissues: skin, cartilage, glue

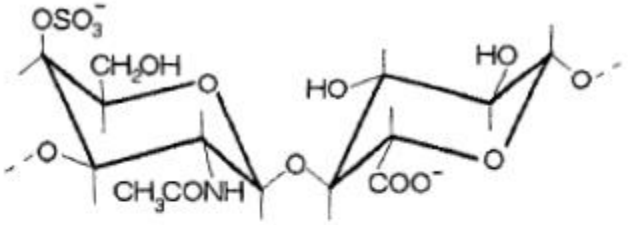
Hyaluronic acid family

Hyaluronic acid (Hyaluronan, HA), is a linear polysaccharide composed of repeating disaccharide units of N-acetyl-glucosamine and D-glucuronic acid. Makes very long chains.

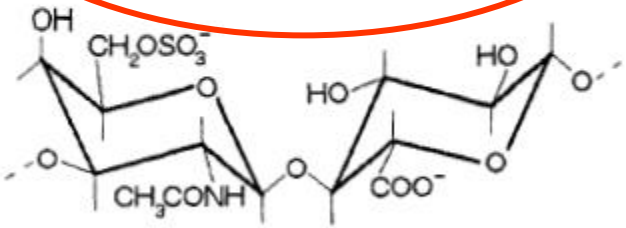
Other members of the HA family: Chondroitin 4 sulphate, chondroitin 6-sulphate, dermatan sulphate



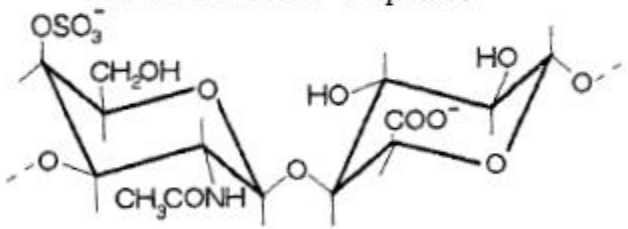
Hyaluronic acid



Chondroitin 4-sulphate



Chondroitin 6-sulphate



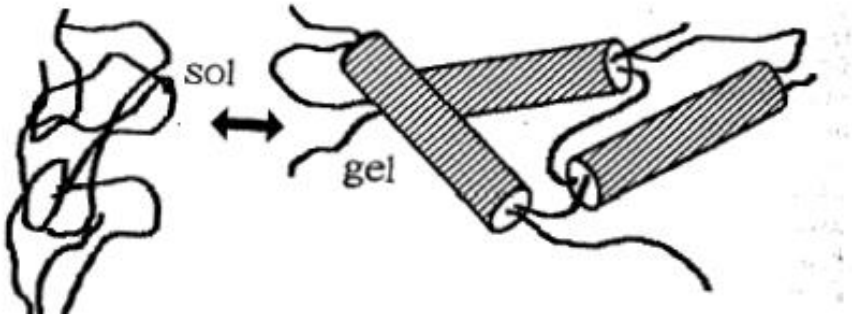
Dermatan sulphate

5. Soft tissues: skin, cartilage, glue

Polysaccharide gels

e.g. Pectins (plant cell wall), Carrageenans, alginates (algae), Glycosaminoglycans (cartilage, synovial fluid), Mucin (mucus)

Gelation: local cross-linking of molecular network



Network formation by hyaluronic acid

Table 3.2 The space-filling ability of hyaluronic acid

Hyaluronic acid (%)	Overlap of molecules (%)
0.02	none
0.1	80
0.5	96

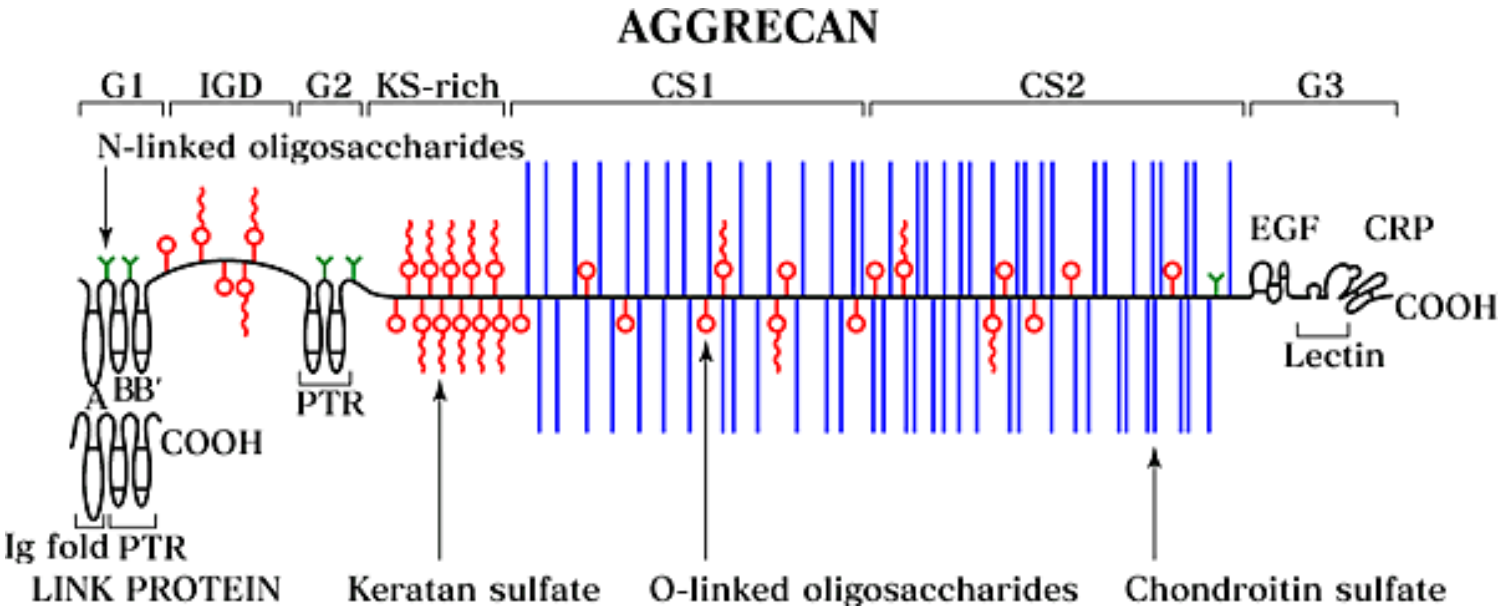
5. Soft tissues: skin, cartilage, glue

Aggrecan

Most abundant proteoglycan in cartilage (90%).

Consists of core protein of high molecular weight (~250,000) + glycosaminoclycan (GAG) chains.

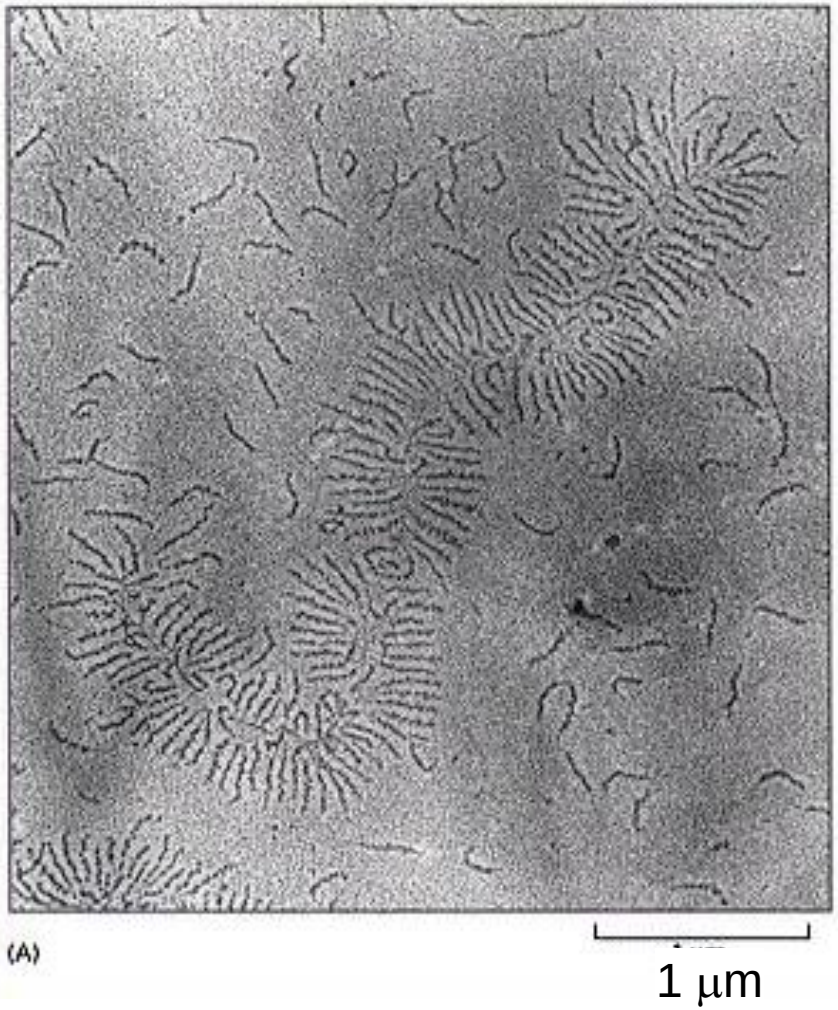
It has 3 globular domains (G1, G2, G3) and 2 extended regions CS1+CS2, where GAGs attach to form branched shape.

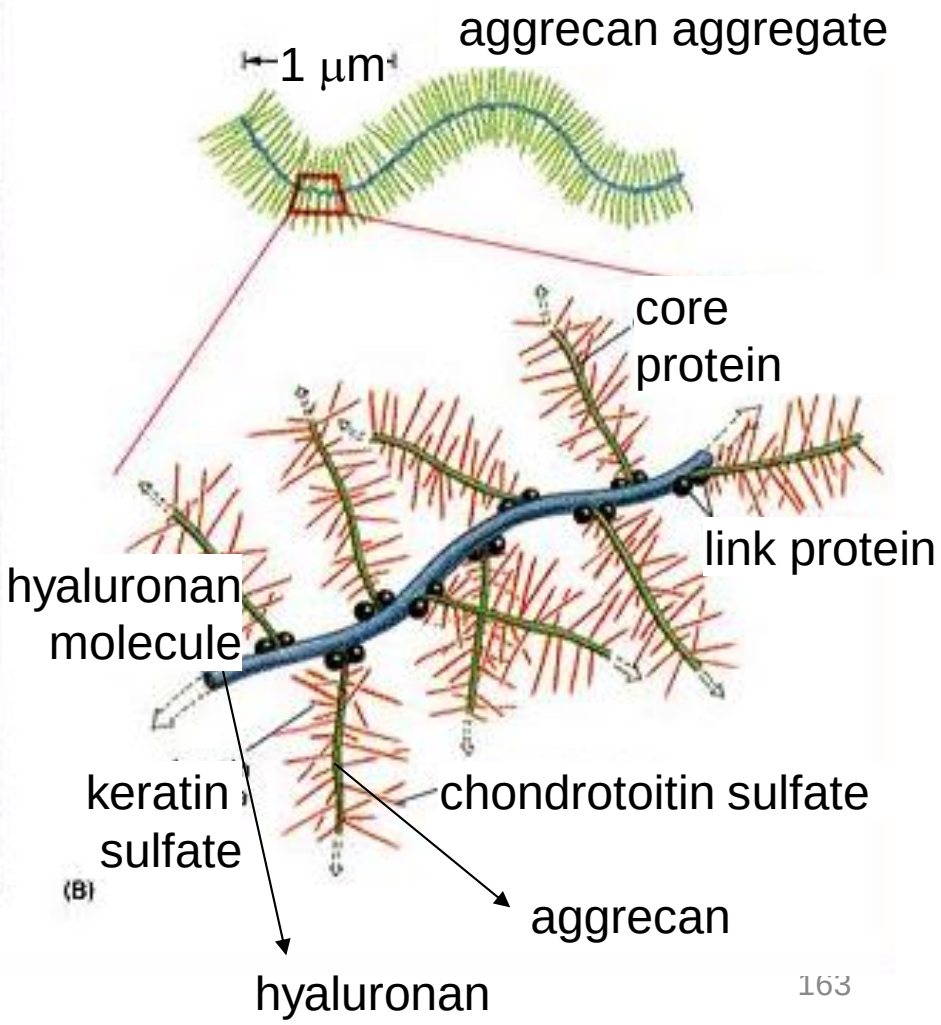


5. Soft tissues: skin, cartilage, glue

Proteoglycan network in cartilage

HA and Aggrecan form huge multimolecular aggregates (around 50 Mio Dalton).



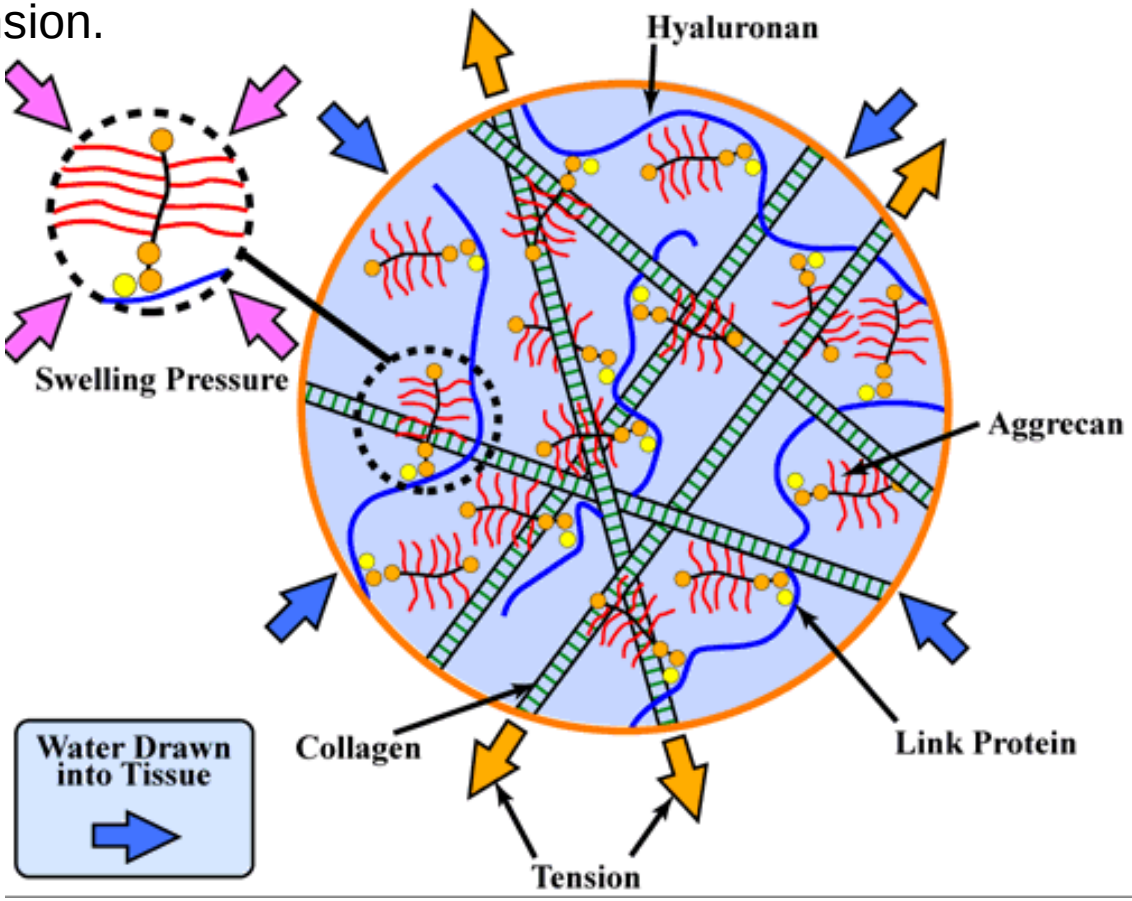


5. Soft tissues: skin, cartilage, glue

Molecular structure of cartilage

Collagen fibers and proteoglycan form network

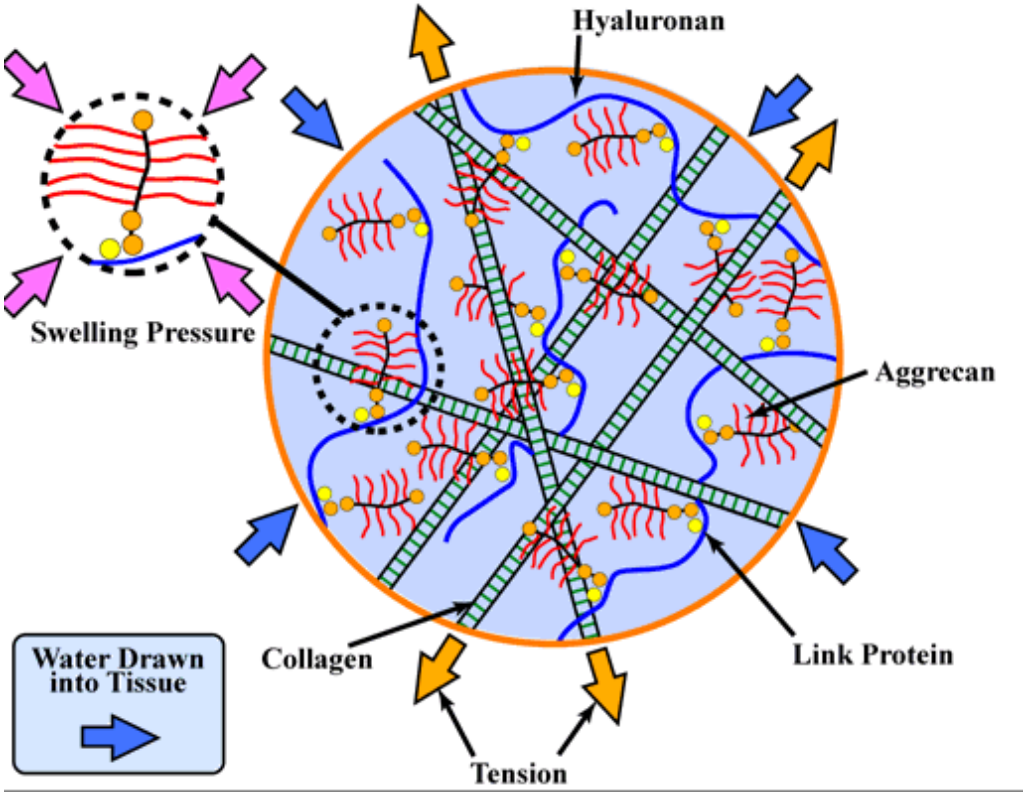
Proteoglycans are hydrophilic, gel imbibes a lot of water by osmosis. Cartilage swells until stopped by max. extensibility of collagen fibers. Collagen fibers pre-stressed in tension.

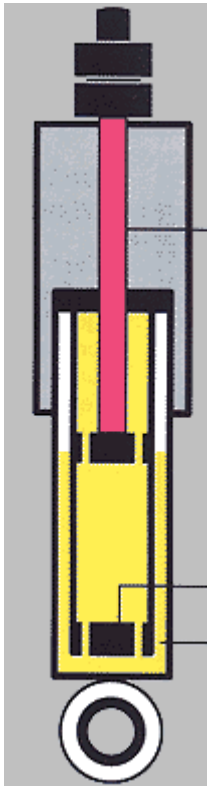


5. Soft tissues: skin, cartilage, glue

Shock absorption

Cartilage: water flows in and out of cartilage during loading and unloading. Shock absorption through viscous flow.





Technical shock absorber

Fluid in joints: synovial fluid (also contains HA), very low coefficient of friction, provides lubricating film

5. Soft tissues: skin, cartilage, glue

5.3 Gastropod pedal mucus

Mixture of polysaccharide gel and non-fibrous protein.

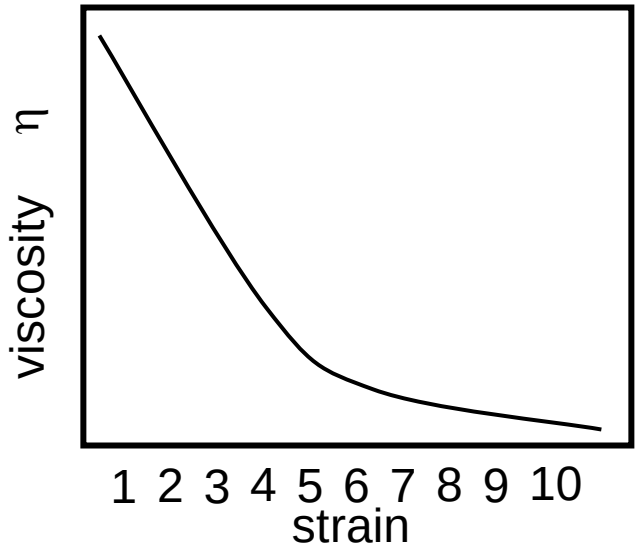
Challenge for slugs on smooth surface (e.g. glass plate):

Stick and slide with same material.

Solution: shear sensitive mucus:

Behaves like a viscoelastic solid at small deformations, at higher deformation rates becomes a rubbery solid. If strained to a factor of 5 or 6, network suddenly breaks down and mucus becomes fluid. Once shear stops, mucus heals, becomes solid again (solid liquid cycle).

Only works in wet state!



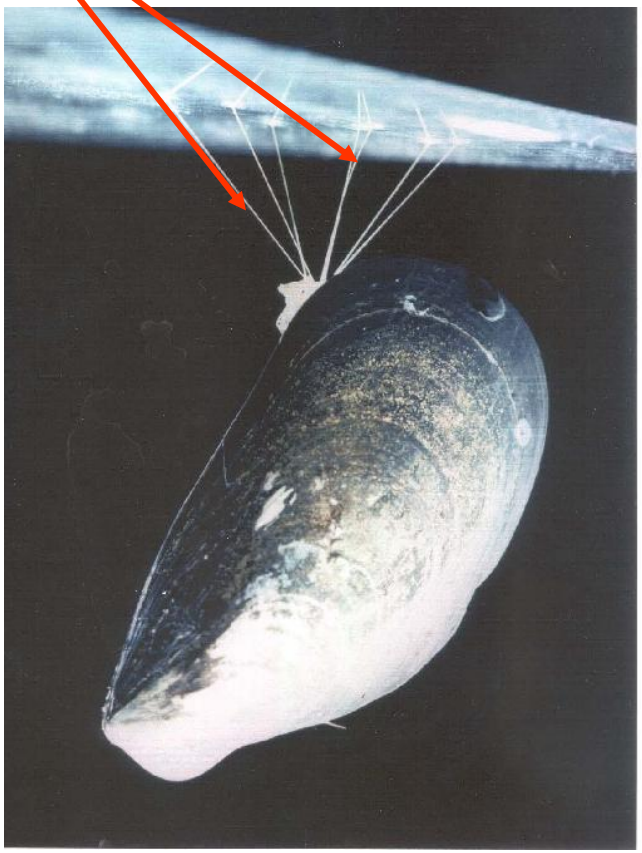
5. Soft tissues: skin, cartilage, glue

5.4 Mussel glue

Challenge for mussles: how to effectively stick to a rock in salt water.

e.g. Mytilis edulis (blue mussel)

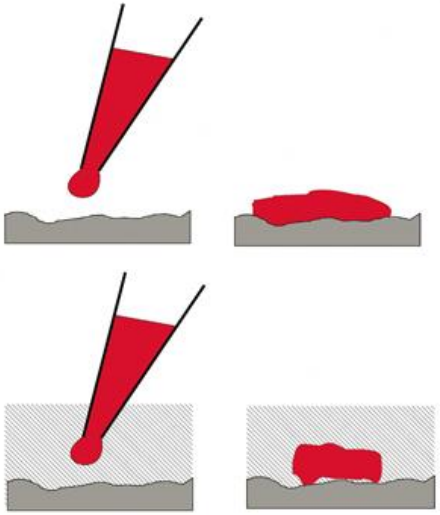
Byssus threads, attach with glue



5. Soft tissues: skin, cartilage, glue

Glue and surface

Conventional glue: use on clean and dry surfaces!



It is easy to place a drop of glue onto a surface in air ...

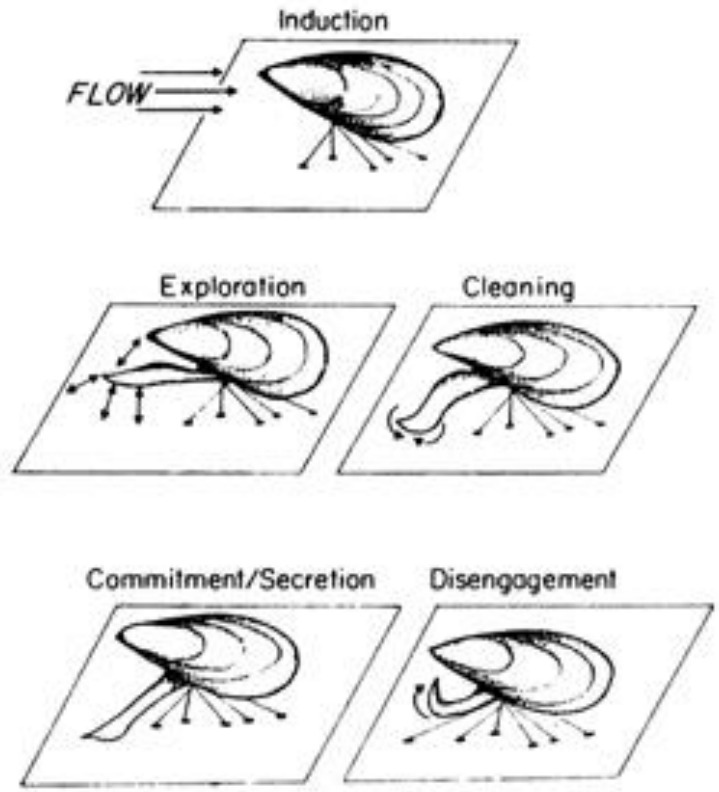
but: not in water!

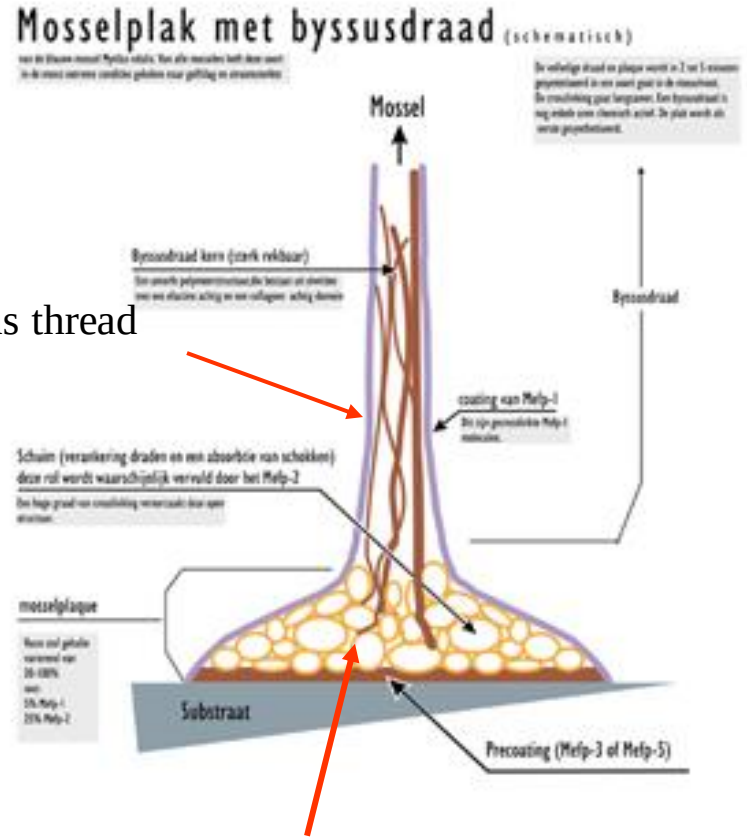
Solution used by mussel: incorporate water into foam-like structure rather than displacing it

5. Soft tissues: skin, cartilage, glue

Mussle plaque secretion

Foot is shaped like suction cup. Part of water is pressed out. Mussle plaque is secreted, rest of water is incorporated in foam like glue structure.





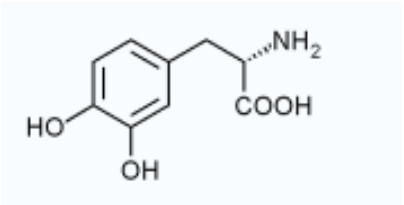
Byssus thread

Drop of glue

5. Soft tissues: skin, cartilage, glue

Gluing in wet and dirty environment

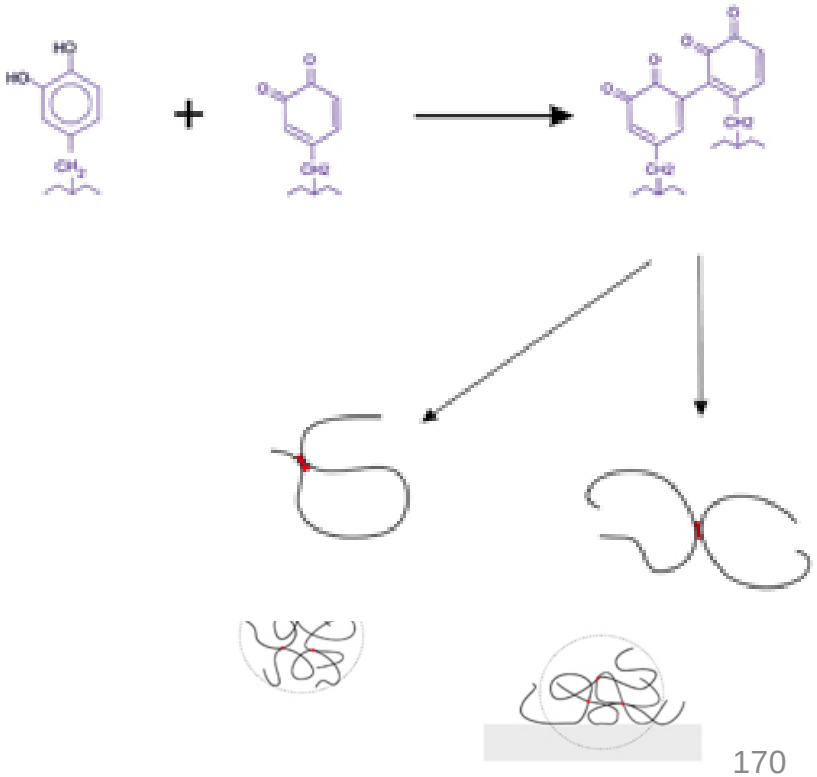
Mussle plaque protein is rich in DOPA – dihydroxyphenylalanine (hydroxylated tyrosine).



The DOPA group can exist in oxidised and non-oxidised form.

They interact and build cross links, in which several chains are linked together, or a single chain links back on itself. A major effect is that the structure changes from linear to branched.

DOPA can also attach to metal (in rock).

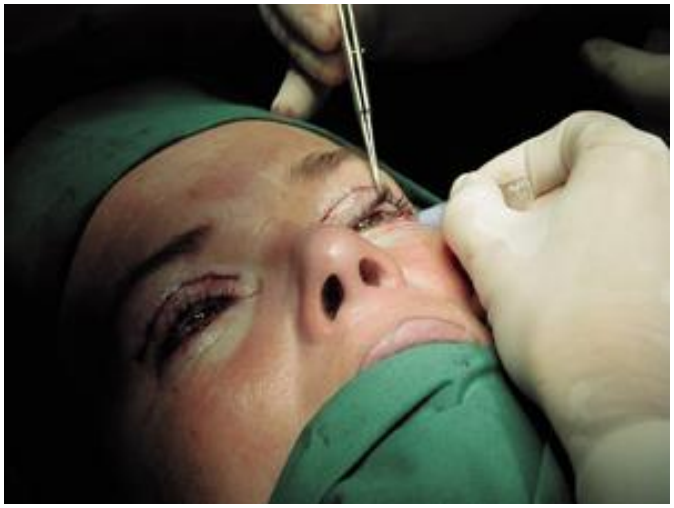


5. Soft tissues: skin, cartilage, glue

Application of mussel-like glue

Gluing in wet and biologically sensitive situations.

Use in medicine and surgery (for small wounds).



5. Soft tissues: skin, cartilage, glue

Summary, soft tissues

Skin: extensibility due to network-like arrangement of collagen fibers

Cartilage:
layered structure of collagen fibers
proteoglycan (macromolecules of protein + sugar) network:
holds huge amounts of water (gel)-> shock absorber

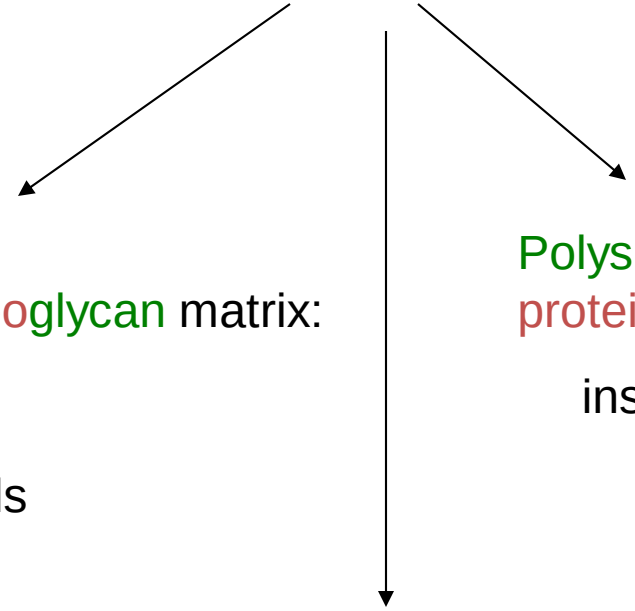
Pedal mucus: highly strain sensitive material (non fibrous protein + sugar)

Mussel glue:
cross-linking through oxidization and metal binding of Dopa

6. Engineering with fibers

Fiber reinforced materials:

Stiff fibers - softer matrix



Protein fibers & polysaccharide/proteoglycan matrix:

- cornea
- tendon
- artery walls
- muscle

Polysaccharide fibers (chitin) & protein matrix:

- insect cuticle

(Polysaccharide fibers & polysaccharide matrix: wood-> Chapter 9)

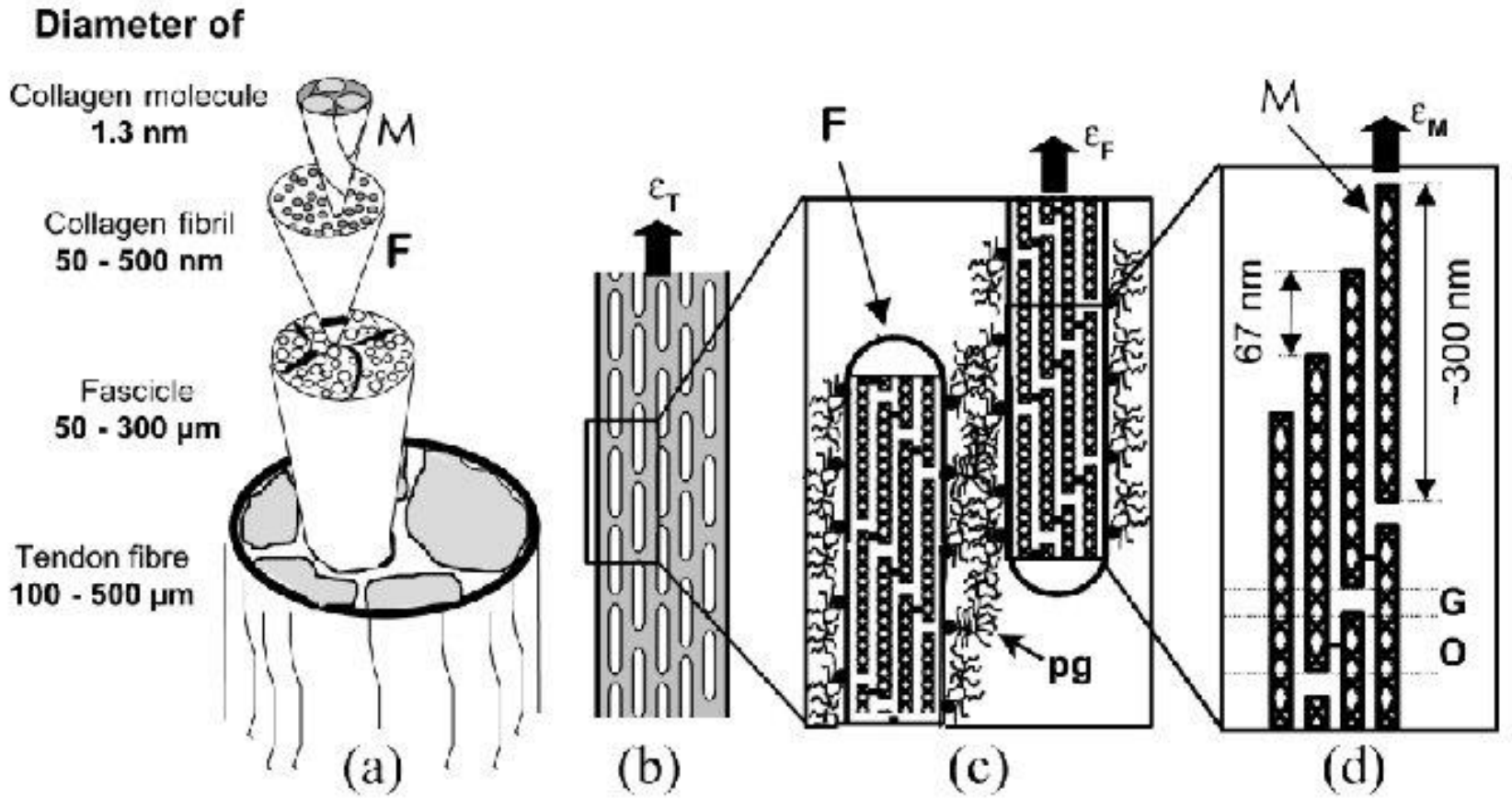
6. Engineering with fibers

6.1 Tendon

Fiber composite: tropocollagen in a hydrated proteoglycan gel.

Loading cycles: healthy humans walk around 1 million steps a year

Hierarchically structured:

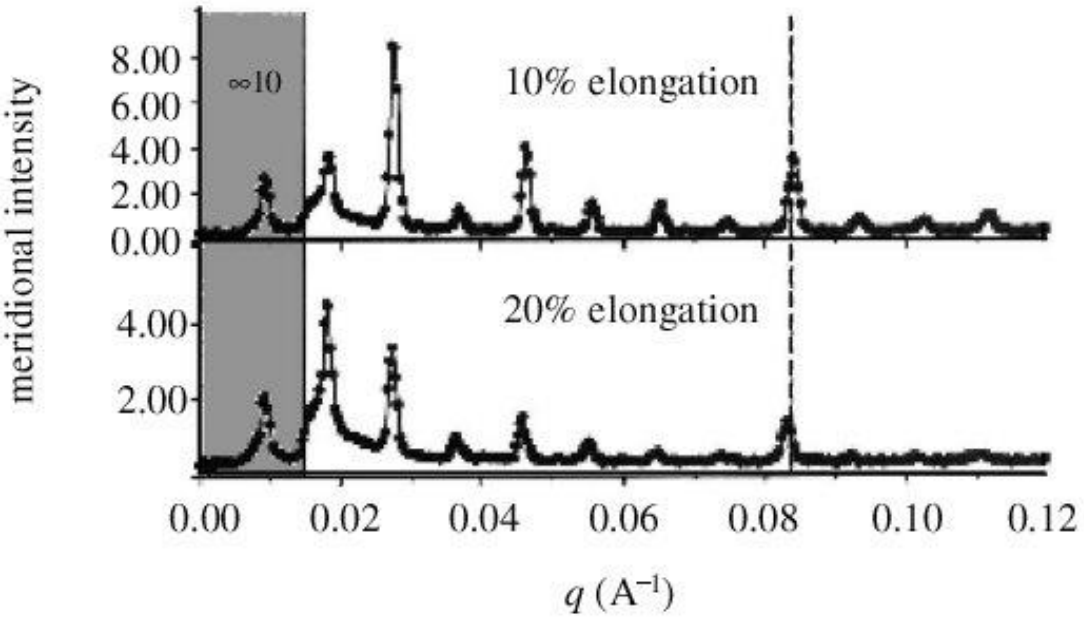


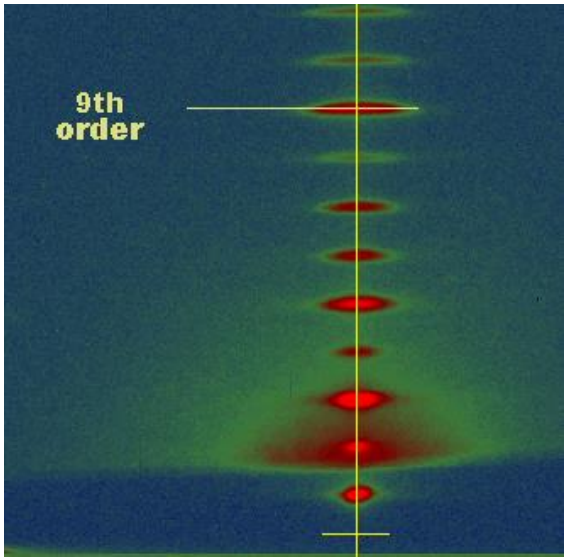
6. Engineering with fibers

Rat tail tendon microstructure

Nanometer scale: regular stacking of collagen molcules, gap and overlap structures (D=67 nm)

Long range order, sharp reflections in X-ray diffraction.



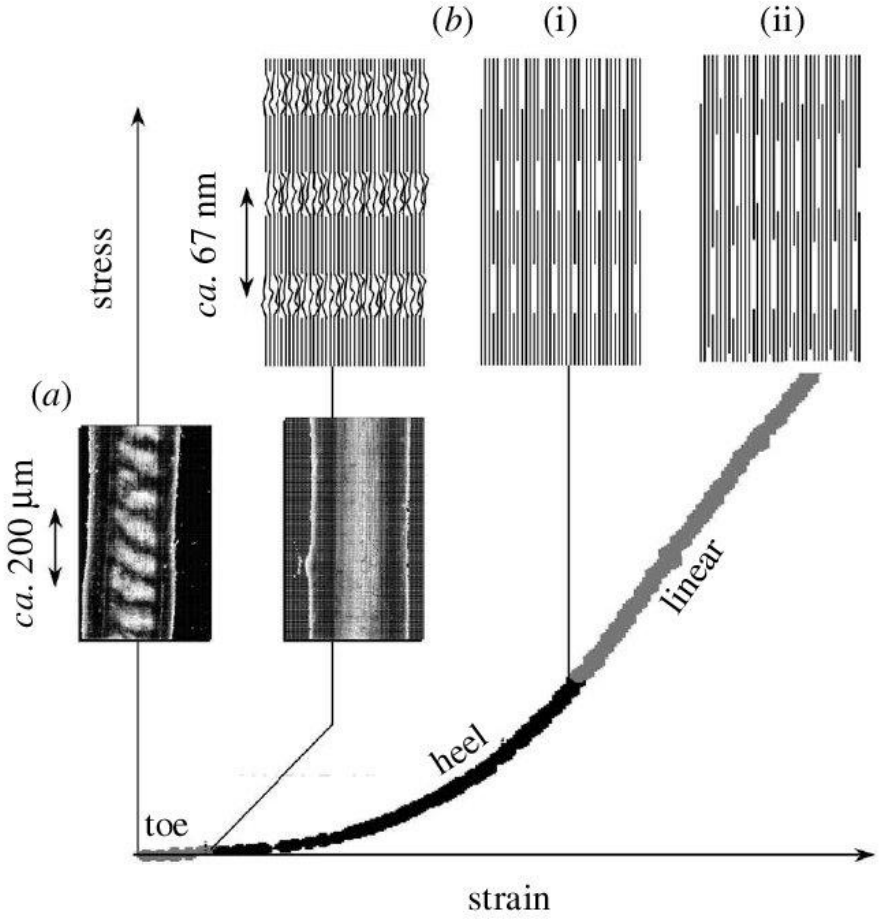


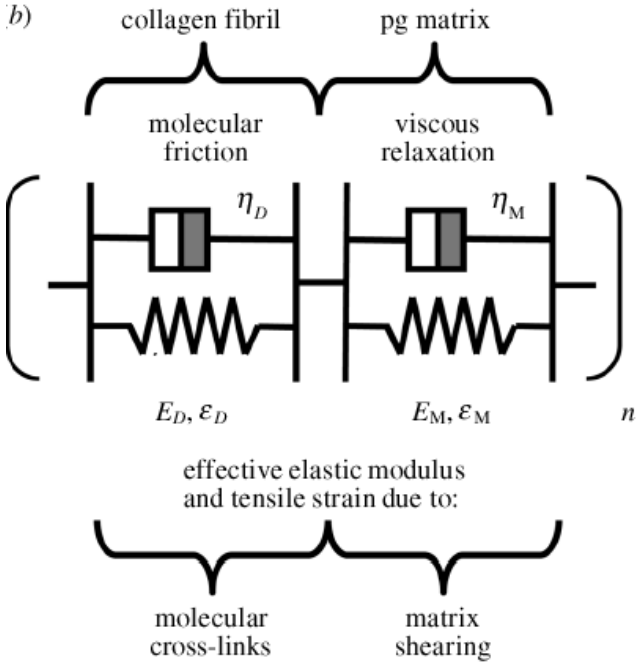
6. Engineering with fibers

Deformation mechanisms in tendon

Typical stress-strain curve of collagen: toe region (unfolding of crimps), heel, hardening: molecules get stretched

→ collagen can be worked in the high strain rate region and low strain rate region



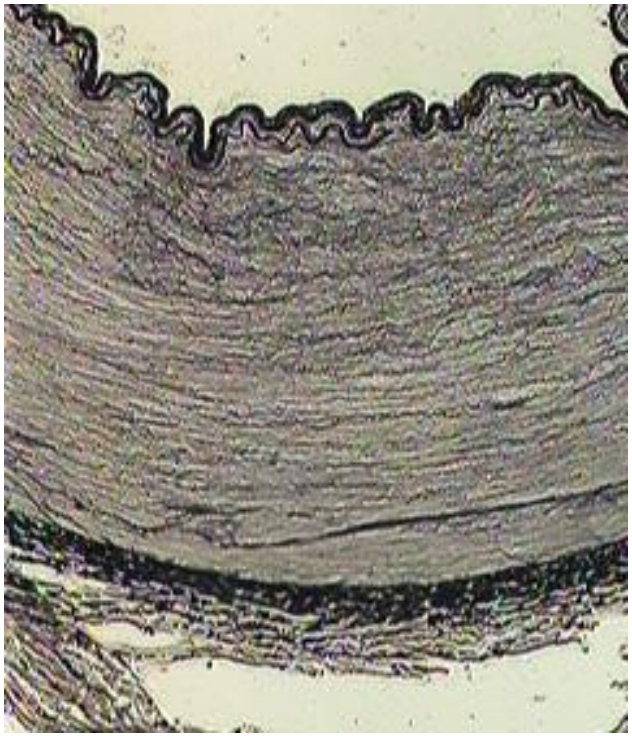


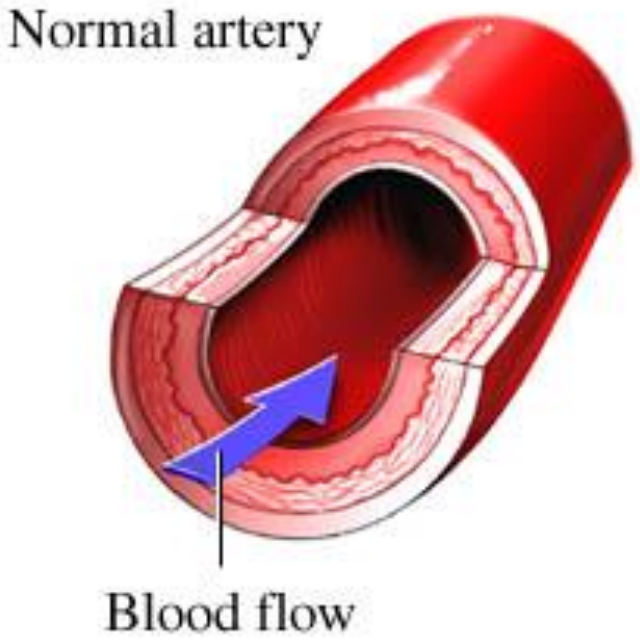
6. Engineering with fibers

6.2 Vascular tissue

Arrangement of collagen fibers: around blood vessel

Has to withstand internal pressure of blood.





6. Engineering with fibers

Microstructure of artery walls

Layered structure, collagen fibers oriented at different angles in adjacent layers.

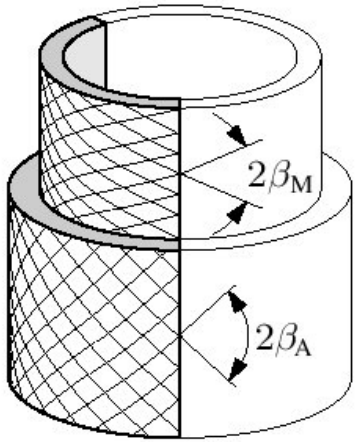


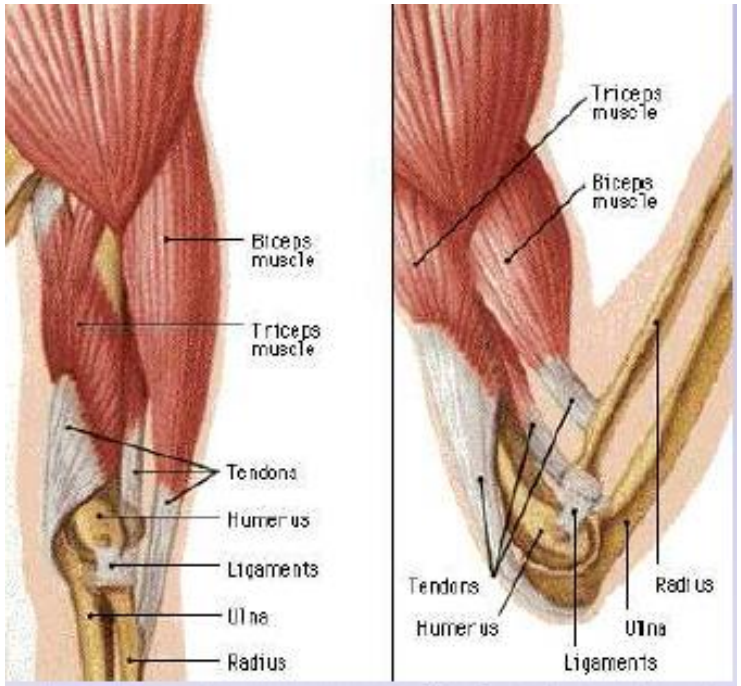
Figure 3: Load-free configuration of an idealized artery modeled as a thick-walled circular tube consisting of two layers, i.e. the media and adventitia.

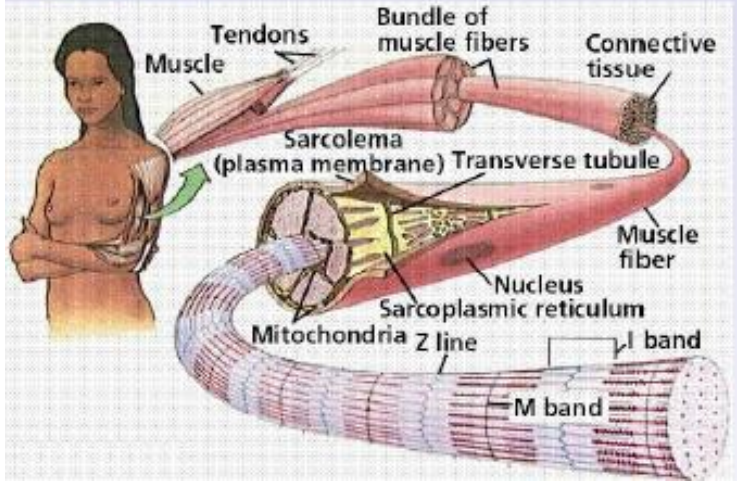
If small slit (up to 5 mm) is introduced in (healthy) aorta wall, and the wall is stretched, the collagen fibers orient across the crack path, effectively stopping it (and preventing catastrophic failure).

Re-orientation is very local, disappears at a distance of only 0.5 mm from the crack tip.

6. Engineering with fibers

6.3 Muscles





General:

Only **tensile forces** possible (muscle contraction only)!
Different modes of motion realized by atagionistic principle: contraction of **extensor/flexor** muscles to increase or decrease angle.

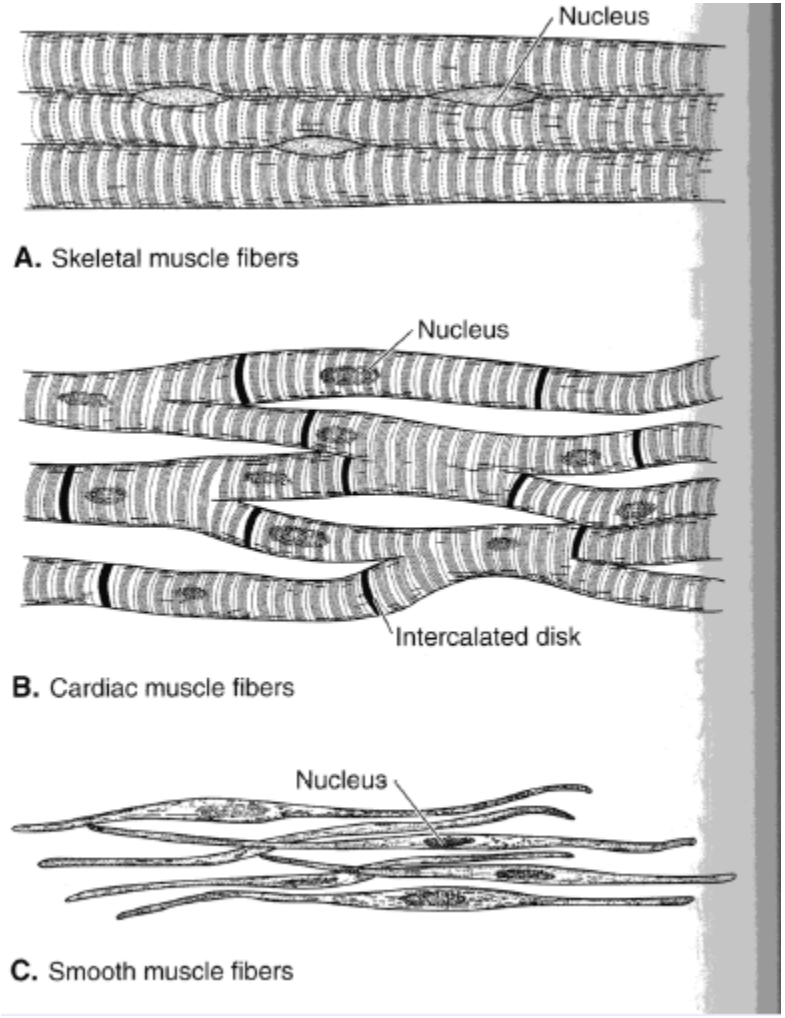
Stress:
constant ca. 250-300 kPa -> force that can be exerted increases with cross-section!

Contraction:
proportional to the fiber length (max. 25% of original length)

Power:
proportional to volume / mass (max. 280W/kg)

6. Engineering with fibers

Types of muscle fibers



Striated muscle:

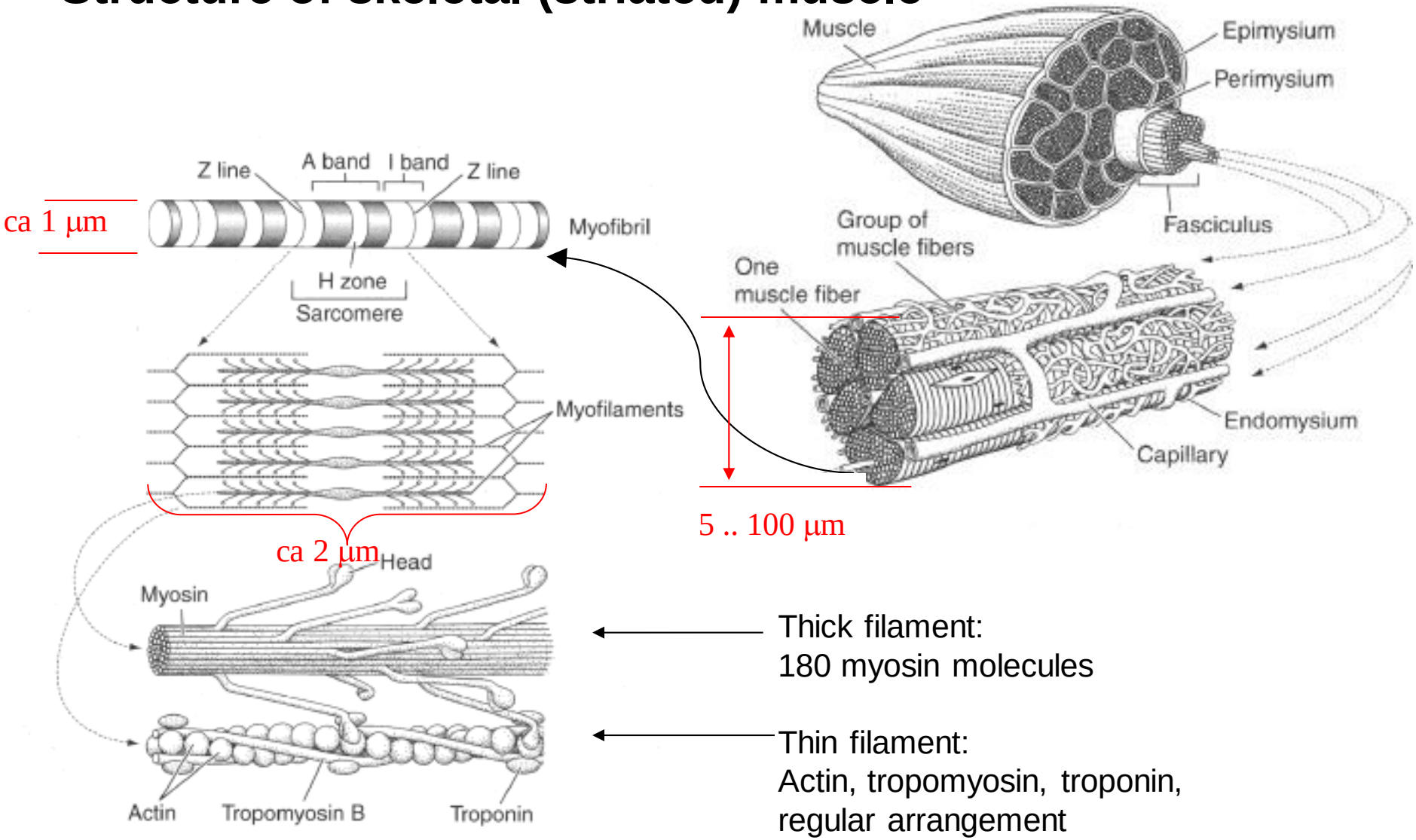
A. Skeletal muscle:
1-30 cm in length
voluntary

B. Cardiac muscle (heart):
80 μm in length
involuntary

C. Smooth muscle
Skin, artery walls, intestine etc.
15-500 μm in length
involuntary

6. Engineering with fibers

Structure of skeletal (striated) muscle

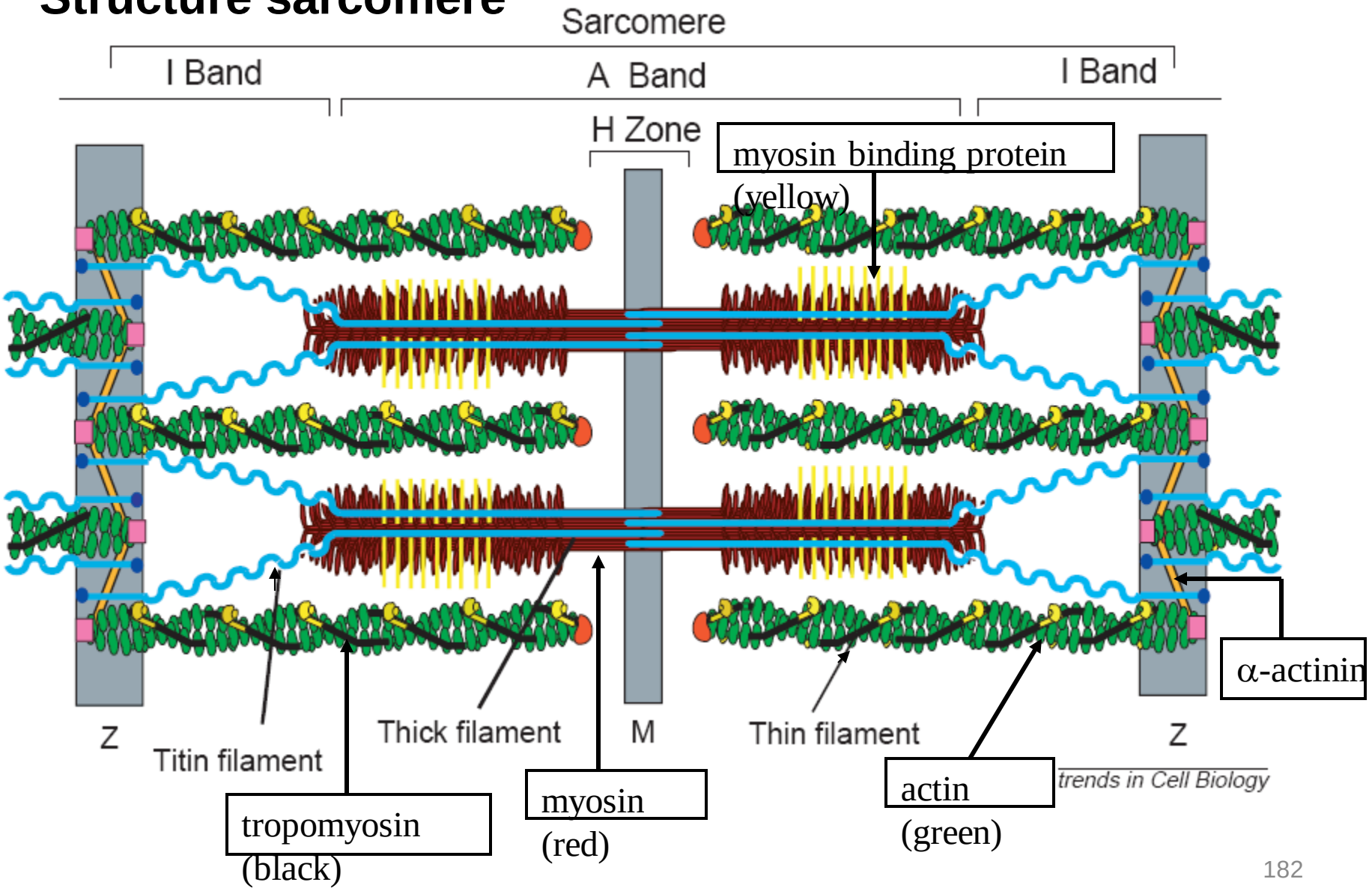


Thick filament:
180 myosin molecules

Thin filament:
Actin, tropomyosin, troponin, regular arrangement

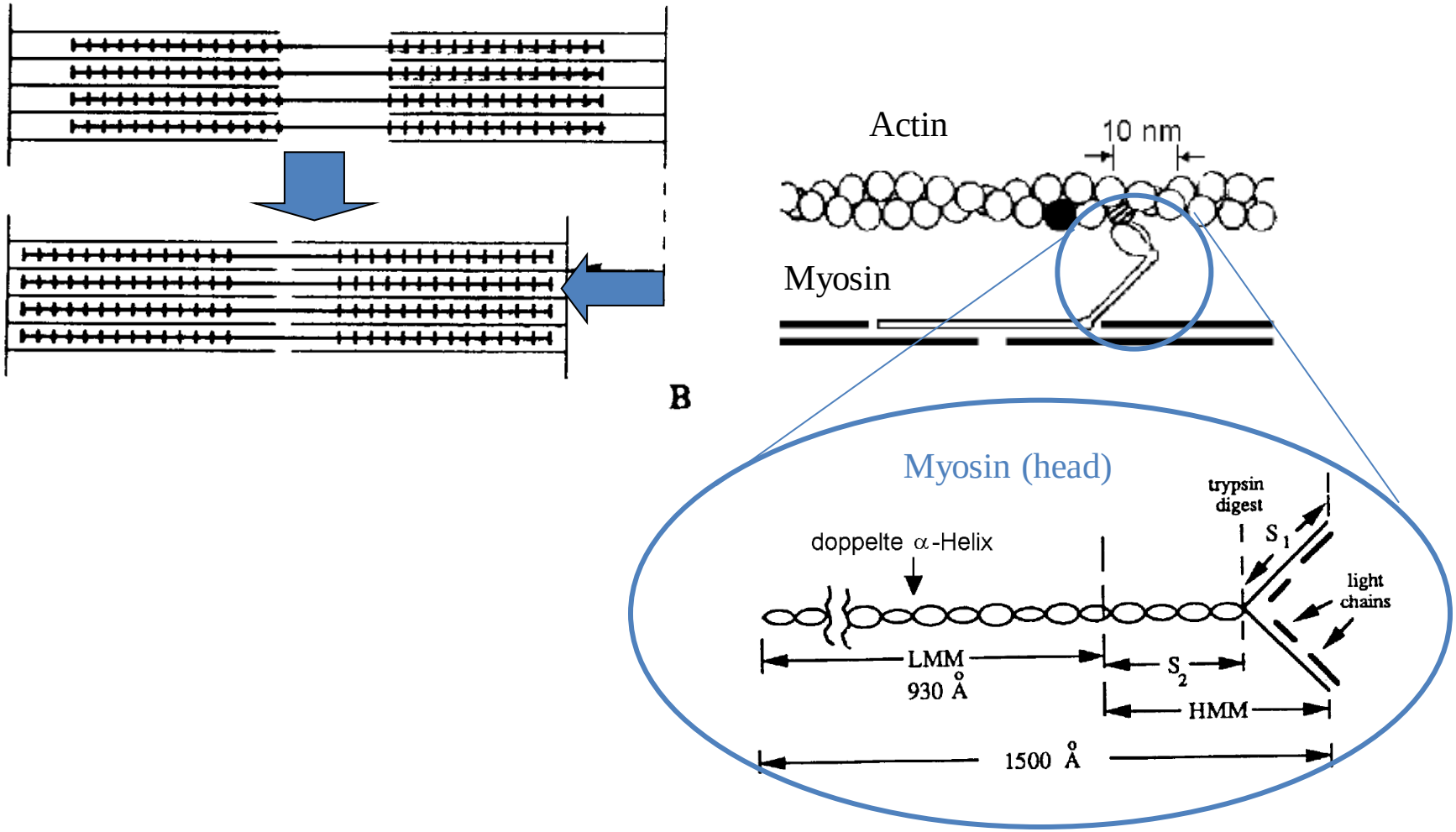
6. Engineering with fibers

Structure sarcomere



6. Engineering with fibers

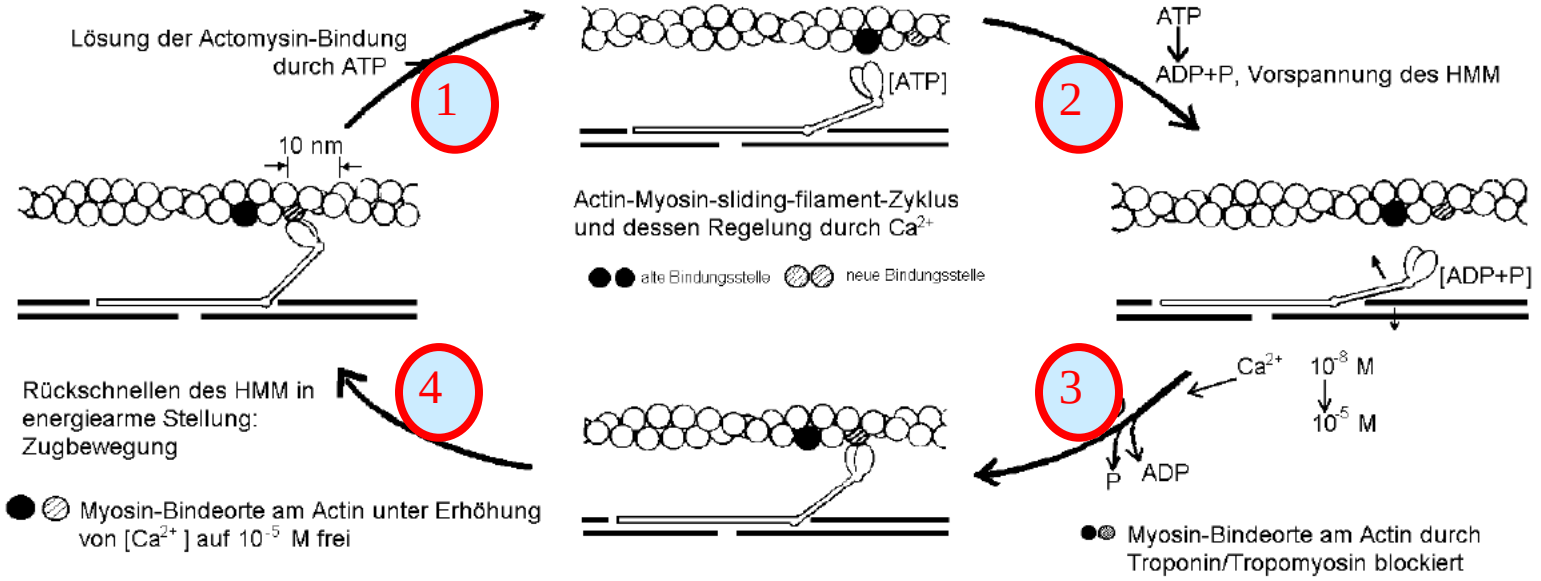
Muscle contraction



heavy mero myosin (HMM): head and part of helix
light mero myosin (LMM): rest of molecule

6. Engineering with fibers

Muscle contraction in detail



1 Myosin heads are detached from actin.

2 Myosin ATPase splits ATP into ADP+P, energy is released; the myosin head absorbs energy, gets pre-stressed and oscillates. Actin binding sites are blocked by tropomyosin / troponin.

3 A nerve impuls sets free Ca2+. The tropomyosin yields HMM binding sites on actin, and the pre-stressed myosin gets bound to actin (actomyosin-ATPase; ADP + P are released).

4 The myosin head snaps back into its energetically favorable, kinked configuration; in this way, the actin slides by about 10 nm with respect to the myosin.

6. Engineering with fibers

Which is the strongest muscle of the body?

Depends on the definition...

If **strong** means

(a) exerting a **maximum force** on an **external object**, then it is the masseter (jaw muscle): max. of 4337 N for 2 seconds (Guinness Book of Records, 1992), not due to muscle size, but due to short lever arm

(b) exerting a **maximum force on the place where it inserts the bone**, then it only depends on the cross section (stress is constant 0.3 MPa). Therefore the “strongest” muscle is usually the quadriceps (front of thigh).

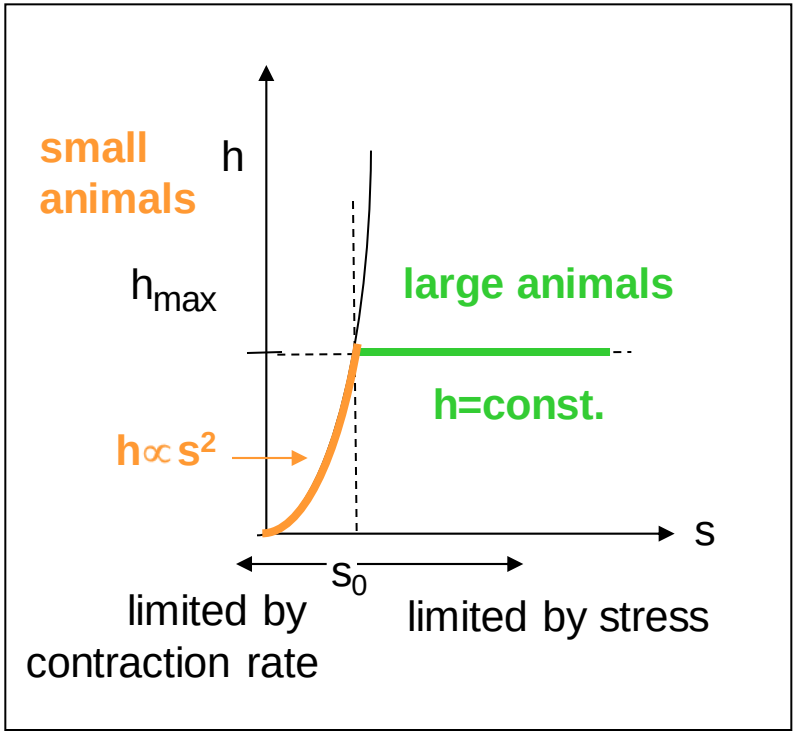
Weight lifting exercise:
What is the minimum muscle size necessary to lift a mass of 50 kg ?

6. Engineering with fibers

Jumping with muscle power, effect of body size

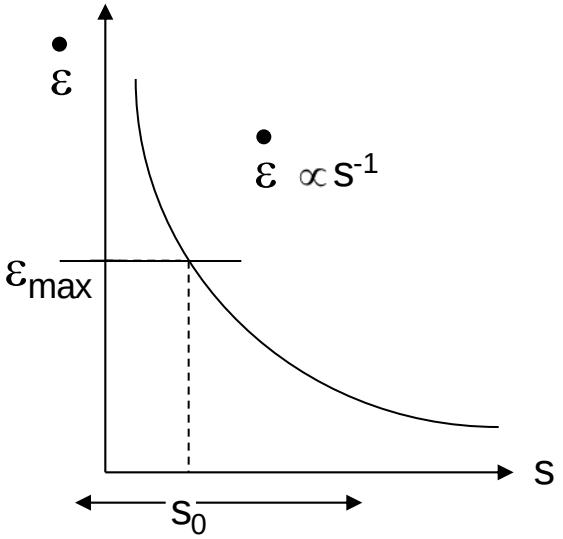
Hill's law, No. 1: jumping height depends on stress

If stress is limiting factor, animals of all sizes could jump to the same height (neglecting air friction and anatomical differences).



Hill's law, No. 2: jumping height depends on contraction rate

If contraction rate is the limiting factor, the jumping height decreases with the square of body size.



$$h \propto \dot{\varepsilon}_{max}^{2} s^2 \Rightarrow h \propto s^2$$

Archibald V. Hill,
1922 Nobel Prize in Physiology or Medicine

6. Engineering with fibers

Jumping flea

THEORY

Hill No. 1

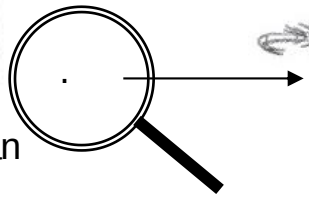
Hill No. 2

REALITY

Human s_H=2m h_H=2m

Flea s_F=2mm h_F=2m

Human s_H=2m h_H=2m



Flea s_F=2mm

Human s_H=2m h_H=2m

Flea s_F=2mm **h_F=20 cm**

Fleas are small animals!

⇨ $h \propto s^2$

$s_H = 1000\ s_F$

$h_H = 10^6\ h_F$

→ **h_F= 2μm**

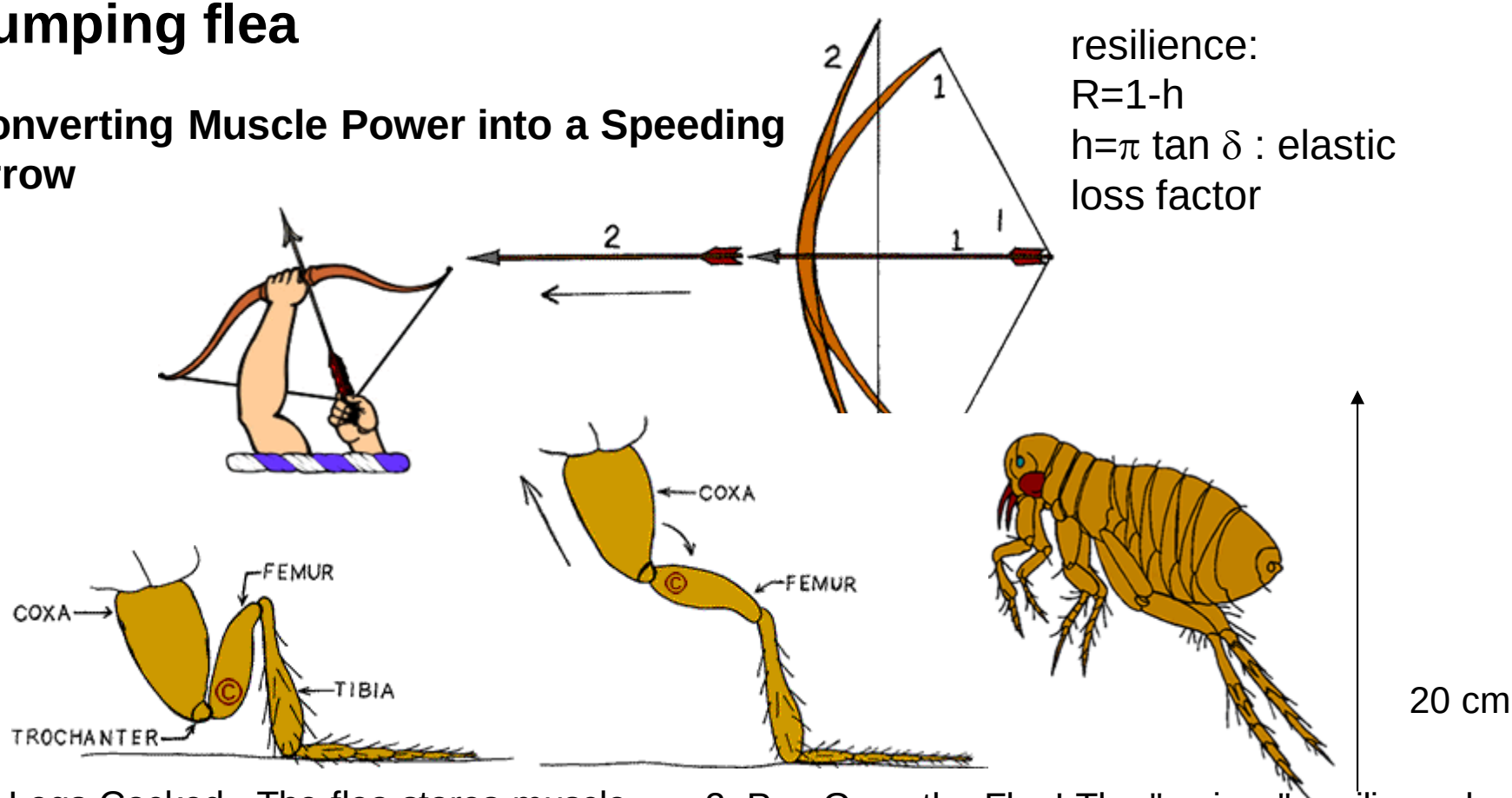
??

6. Engineering with fibers

Jumping flea

Converting Muscle Power into a Speeding Arrow

resilience:
R=1-h
h=π tan δ : elastic loss factor



1. Legs Cocked - The flea stores muscle energy in a resilin pad inside the coxa (looks kind of like a thigh). Resilin is an elastic (or "springy") material. Resilin is one of the best materials known for storing and releasing energy efficiently.

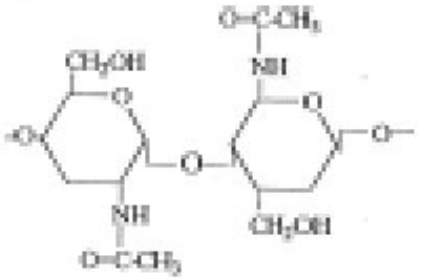
2. Pop Goes the Flea! The "springy" resilin pad releases the energy and opens the leg much faster than the muscles can. The legs push the flea away from the ground and the flea accelerates (speeds up) upward at a high speed.

6. Engineering with fibers

6.4. Insect cuticle

Insect cuticle: major constituents

- **Chitin** (25-40% by wt) -- first isolated from insects in 1823; a 50-1000 until polymer (chain) of N-acetylglucosamine; chains are bound by proteins to form sheets or lamellae; lamellae are laid down at different angles every half hour – makes the cuticle non-stretchable; approx. 85% of chitin in the cuticle is resorbed between molts



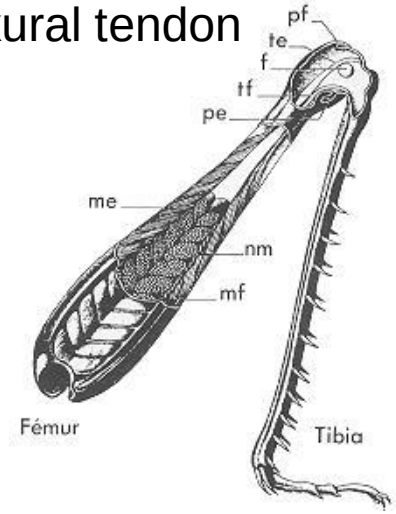
chitin

- **Proteins** (≥50% by wt) – cross-linked to chitin lamellae, but type and degree of cross-linking is not understood. One special protein is *resilin*, a natural elastiomer that can stretch 30X its length.

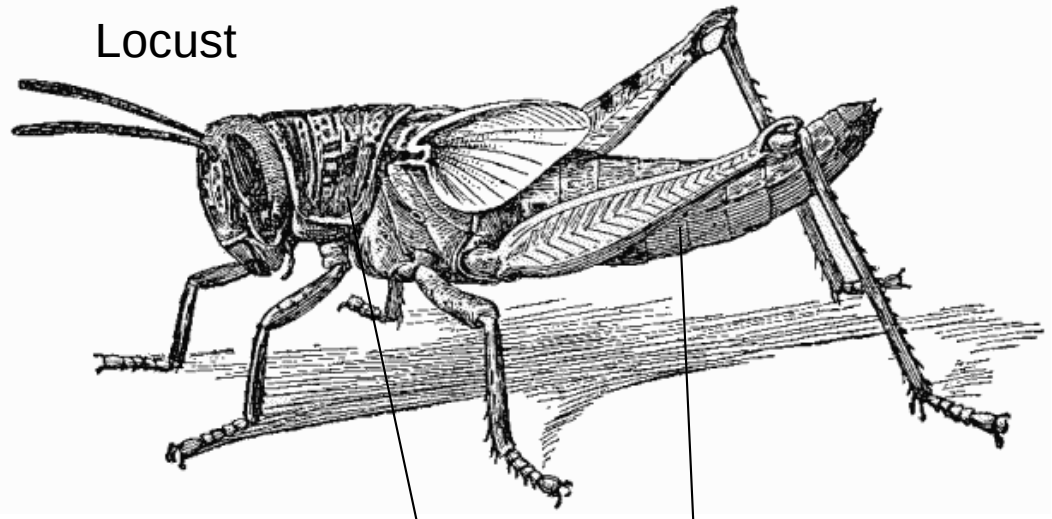
6. Engineering with fibers

Orientation of chitin in insect cuticle

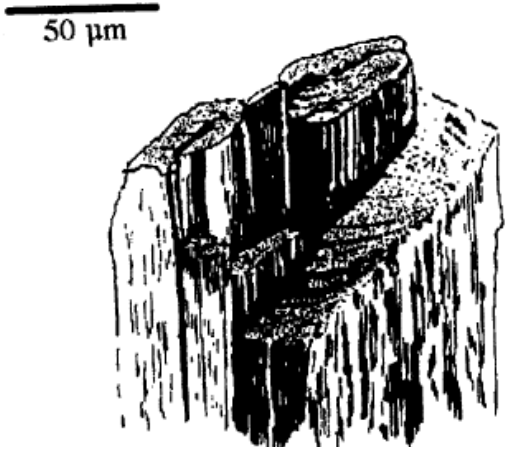
tf: flexural tendon



Locust

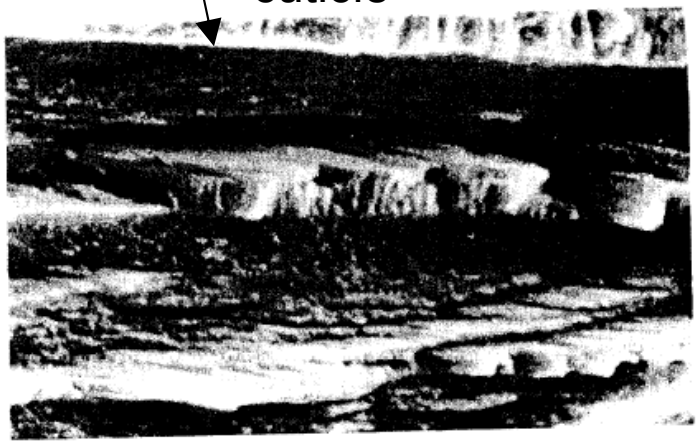


locust tendon



The broken end of a locust tendon.

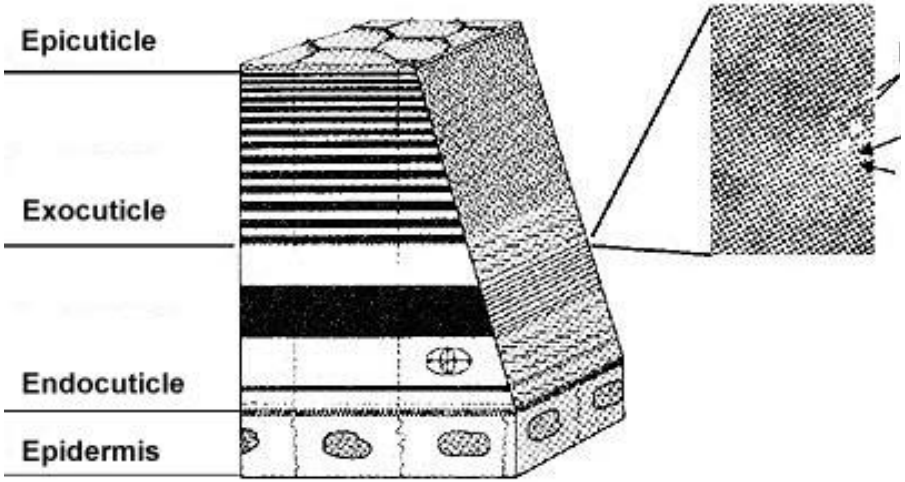
cuticle



Typical fracture surface of a cuticle with layers.

6. Engineering with fibers

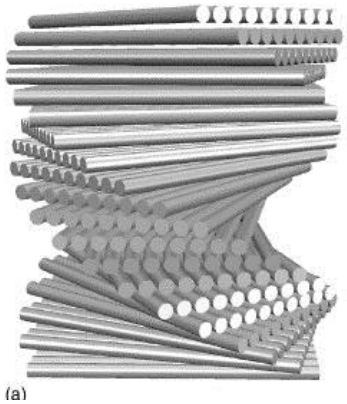
Layered structure of insect cuticle



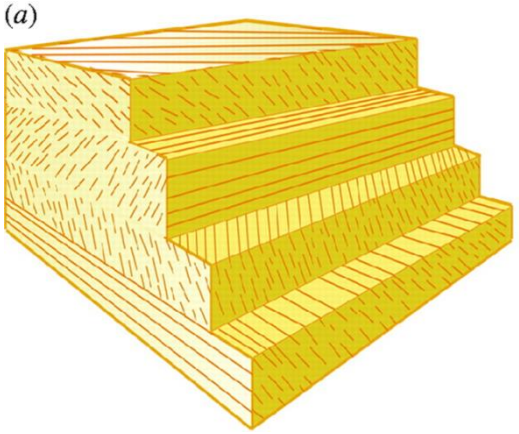
protein matrix

Chitin fibrils
(2.8 nm diameter)

Chitin fibers in helicoidal arrangement:



Sketch of helicoidal chitin fiber arrangement in lobster cuticle. From: D. Raabe et al., *Mat. Sci. Eng. A* 421 (1-2), 143-153, 2006.



Crysina boucardi, scarab beetle. From: Seago A E et al. J. R. Soc. Interface 2009;6:S165-S184

6. Engineering with fibers

Chitin fibril in cross section

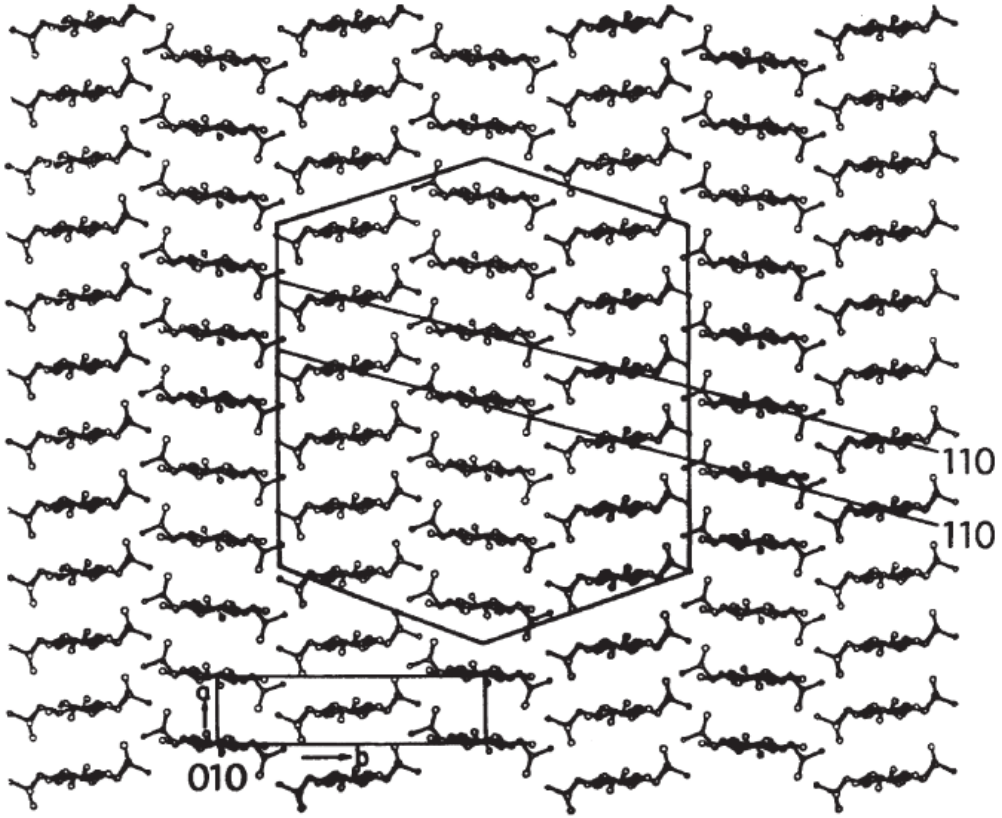


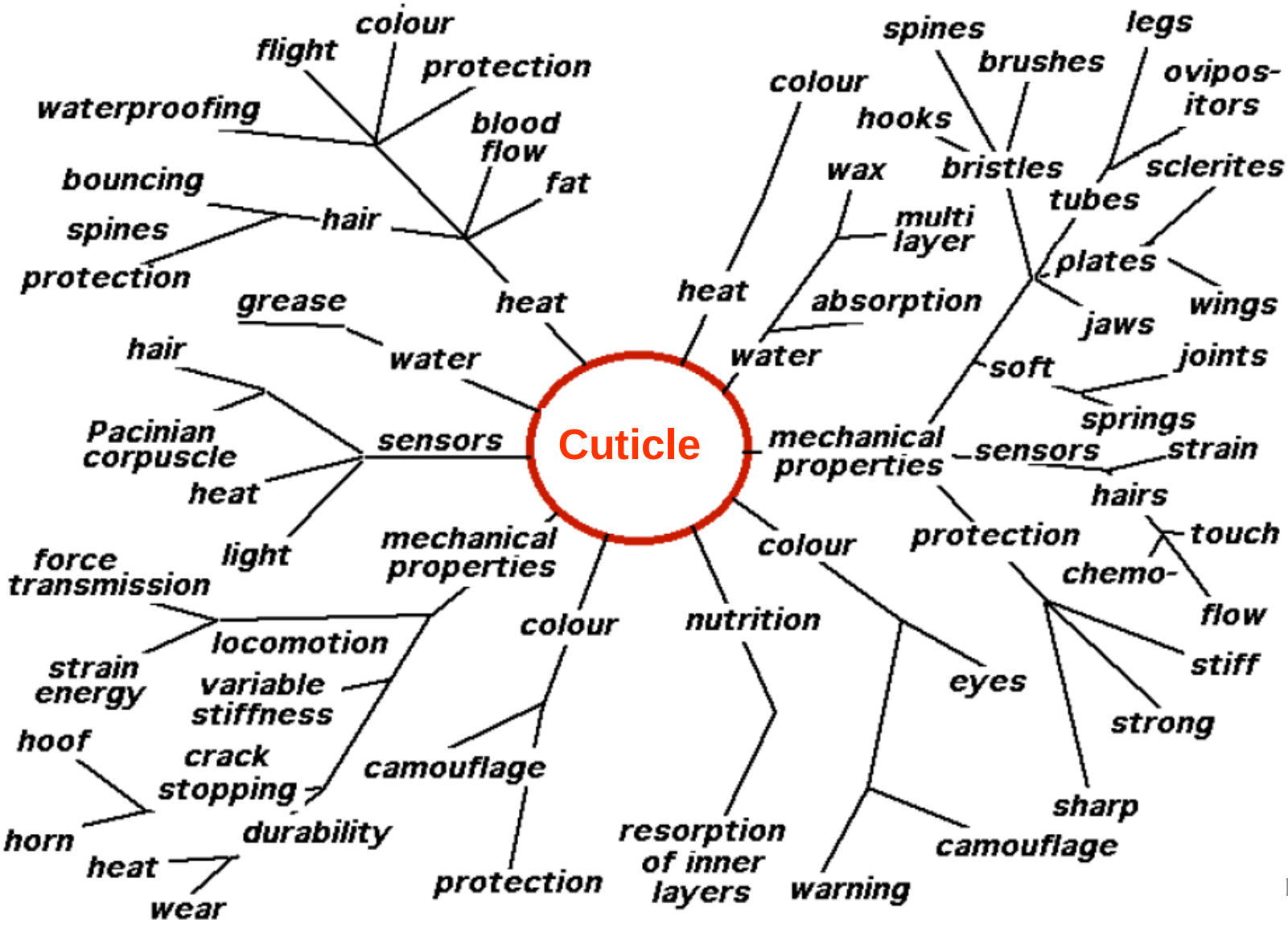
Fig. 1. End view of a chitin crystallite showing the typical section of a chitin nanofibre looking along the chitin chains which are extending out of, and into, the page in order to create the nanofibre.

Highly crystalline, stiff, E= ca. 150 GPa
Used in fiber composite with protein matrix.

J.F.V. Vincent and U.G.K. Wegst (2004). Design and mechanical properties of insect cuticle. *Arthropod Structure & Development* **33** (3), 187-199.

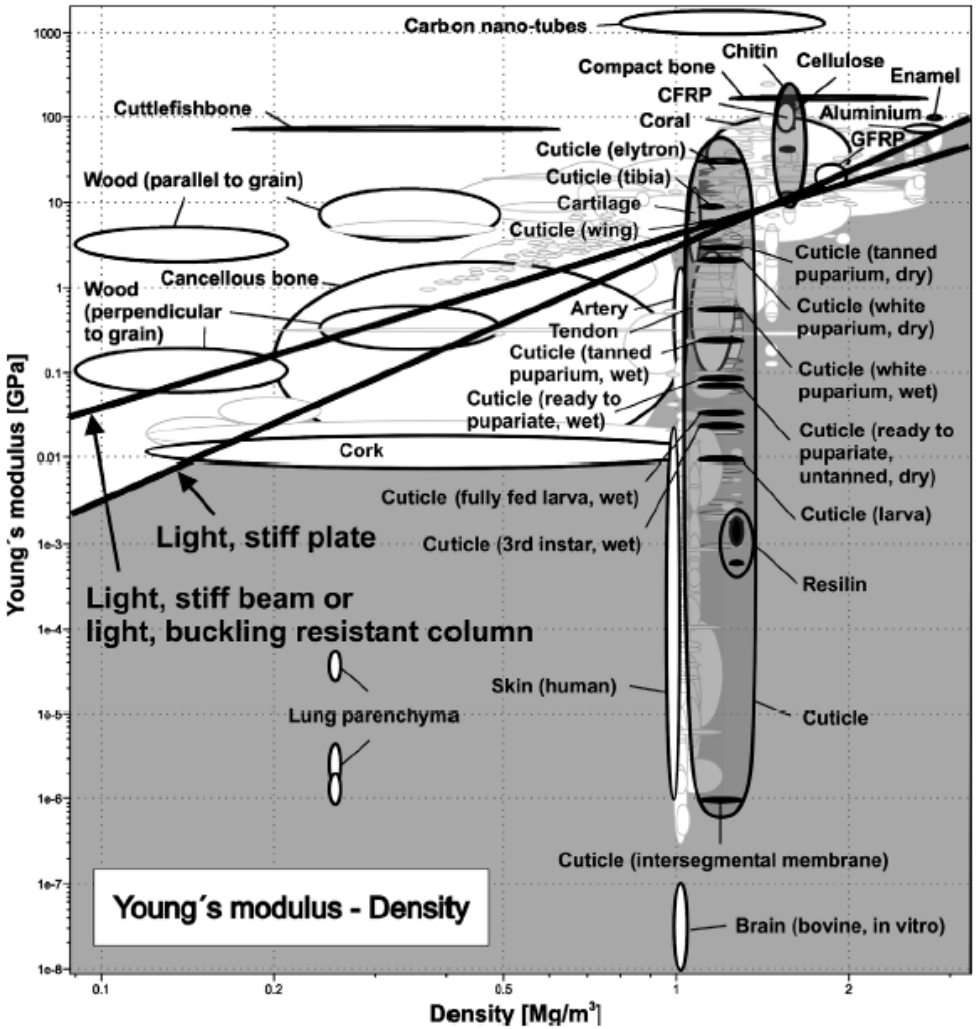
6. Engineering with fibers

Tasks of insect ctuticle



6. Engineering with fibers

Stiffness of chitinous cuticle



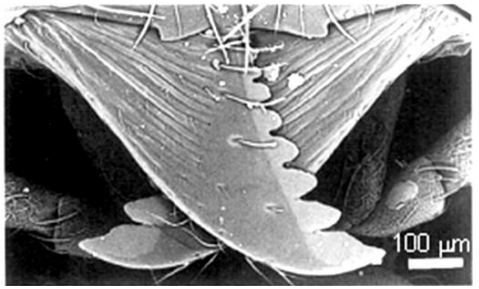
J.F.V. Vincent and U.G.K. Wegst (2004). Design and mechanical properties of insect cuticle. *Arthropod Structure & Development* **33** (3), 187-199.

6. Engineering with fibers

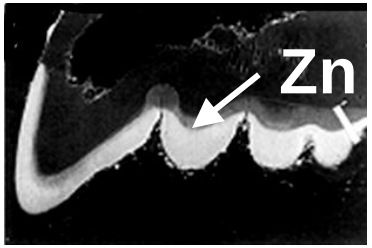
Varying mechanical properties by

- Type of protein (chemistry, MW)
- Chitin/protein ratio
- Orientation of chitin
- Amount of water / degree of tanning
- Presence of lipids, salts, etc
- Added metals (Zn, Mn)
- Added $CaCO_3$

Mandible of leaf cutter ant



e.g. in some wasps

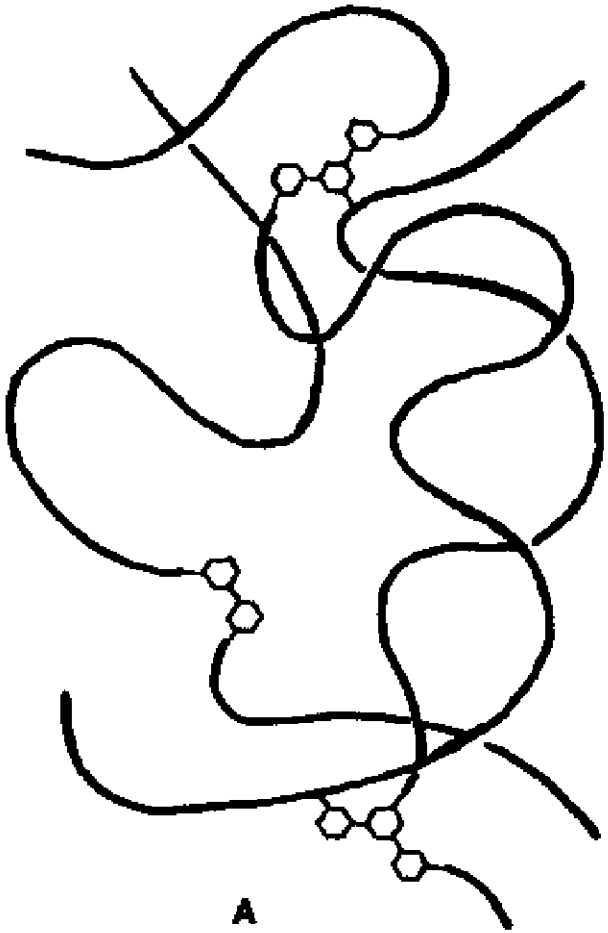


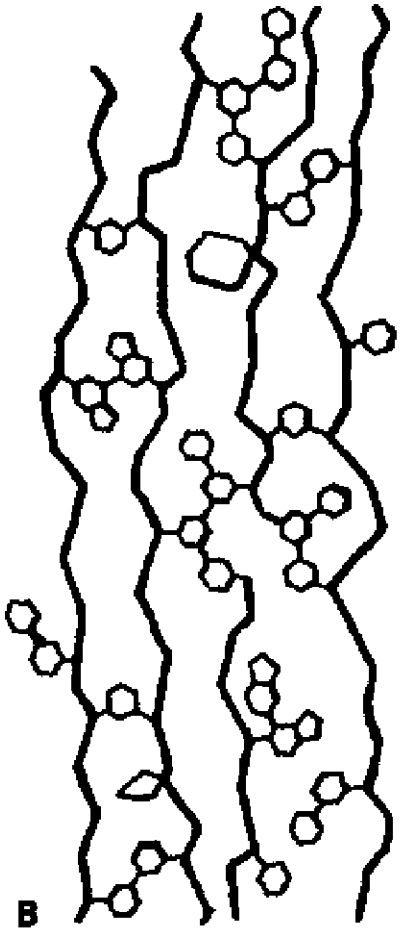
6. Engineering with fibers

Protein matrix

Resilin

Sclerotin



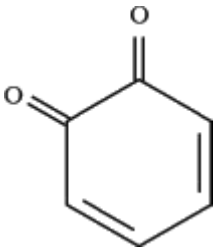


hydrophilic

hydrophobic

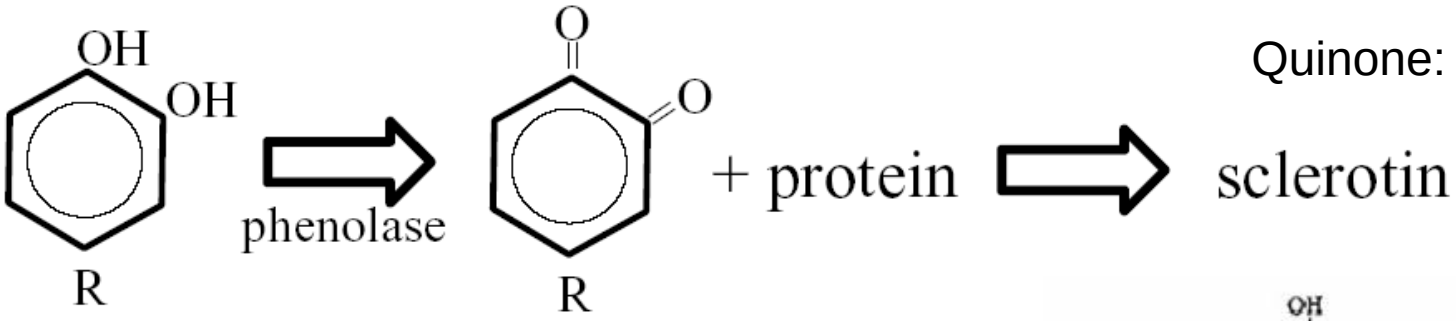
6. Engineering with fibers

Stiffening cuticle

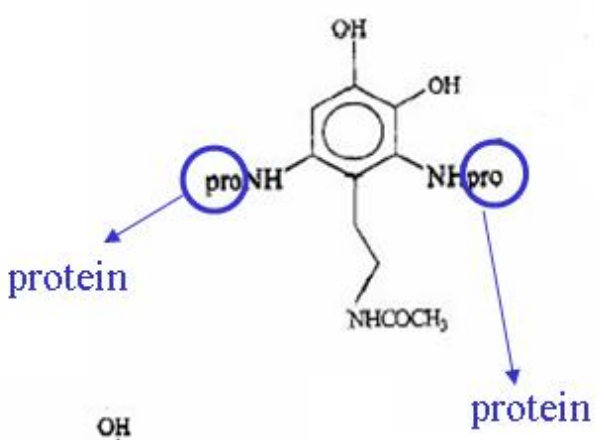


Quinone: $C_6H_4O_2$

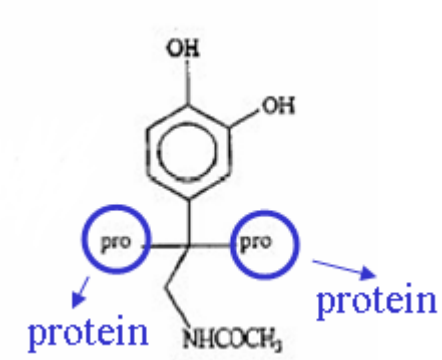
Tanning: chemically harden the exocuticle through cross-linking of cuticular proteins with oxidized phenols (sclerotization):



1. Quinone tanning (quinones used for tanning leather, fabrication of dyes, photography...), dark color



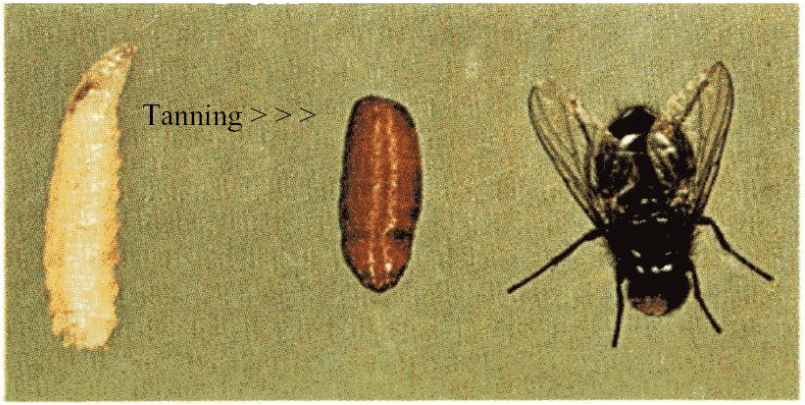
2. β-sclerotization (often resulting in light color)



6. Engineering with fibers

Tanning

Maggot – Puparium - Fly



Molting insect

After molting: cuticle is still untanned (soft), insect very vulnerable (to predators, insecticides, etc.) during this time. Tanning process can take up to six hours.

6. Engineering with fibers

Tanning and mechanical properties

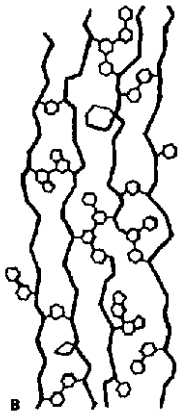
Tanning = cross-linking of protein matrix -> cuticle stiffer
BUT: same effect can be obtained by drying untanned (or less heavily tanned) instect cuticle

Conclusion: Effect of tanning is mainly **dehydration** by controlling the **degree of hydrophobicity** via degree of cross-linkin.

Soft (compliant) cuticle, more hydrophilic:
40-75 % water (composition of dry cuticle: ca. 50% wt chitin, 50% protein)

Hard (stiff), more hydrophobic:
ca. 12 % of water (composition of dry cuticle: 15-30% wt chitin, rest protein)

REMEMBER: matrix proteins



sclerotin
(hydrophobic)

6. Engineering with fibers

Functions of tanning in insect cuticle

- mechanical protection
- water retention/conservation
- protective barrier against bacteria, viruses, toxins (incl. pesticides)
- location of colors and patterns [important in behavior (avoiding predation, mating)]

6. Engineering with fibers

Summary – Engineering with fibers

Tendons: collagen fiber composite of hierarchical structure. Shows typical toe-heel curve upon deformation.

Artery walls: collagen fibers wound concentrically around blood vessel, layers with different orientation, high toughness and crack tolerance.

Muscle: skeletal muscle is a protein fiber composite from mainly myosin and actin. Muscle contraction: relative movement of thick filament (myosin) and thin filament (actin) through movement of myosin head ("myosin motor").

Insect cuticle: chitin fibers in protein matrix. Huge variation in stiffness at very similar composition. Mechanical tuning by fiber orientation, water content and tanning.

7. Bioceramics

Biomineralization

Definition: controlled deposition of mineral/salt (*inorganic*) in the body of a living organism

History:

Biomineralization started probably around 3500 million years ago (age of earth: about 4200 million).

Skeletal hard parts: only 570 million years ago.

Tasks of mineralized tissue:

- protection
- motion
- cutting and grinding
- buoyancy
- optical, magnetic and gravity sensing
- storage

7. Bioceramics

Mineralization versus purely organic

Hard parts: can be obtained

- on the basis of purely organic material
- by filling organic matrix with mineral

Both strategies may be found in one phylum, e.g. arthropods

7. Bioceramics

Hard parts production in nature and technology

No metals

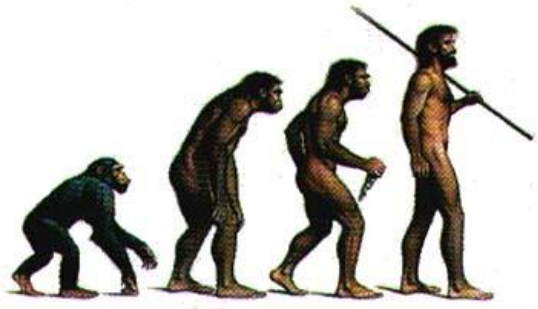
stone, bones

Homo Sapiens, Celebrating Their Diversity...

Metals

advantages of metals: malleable, ductile, don‘t break easily, strong

time



Remember: no hard parts from pure metals in biology – why?

7. Bioceramics

Mechanical performance, metal - bioceramics

Plastic deformation in mild steel and cow bone:

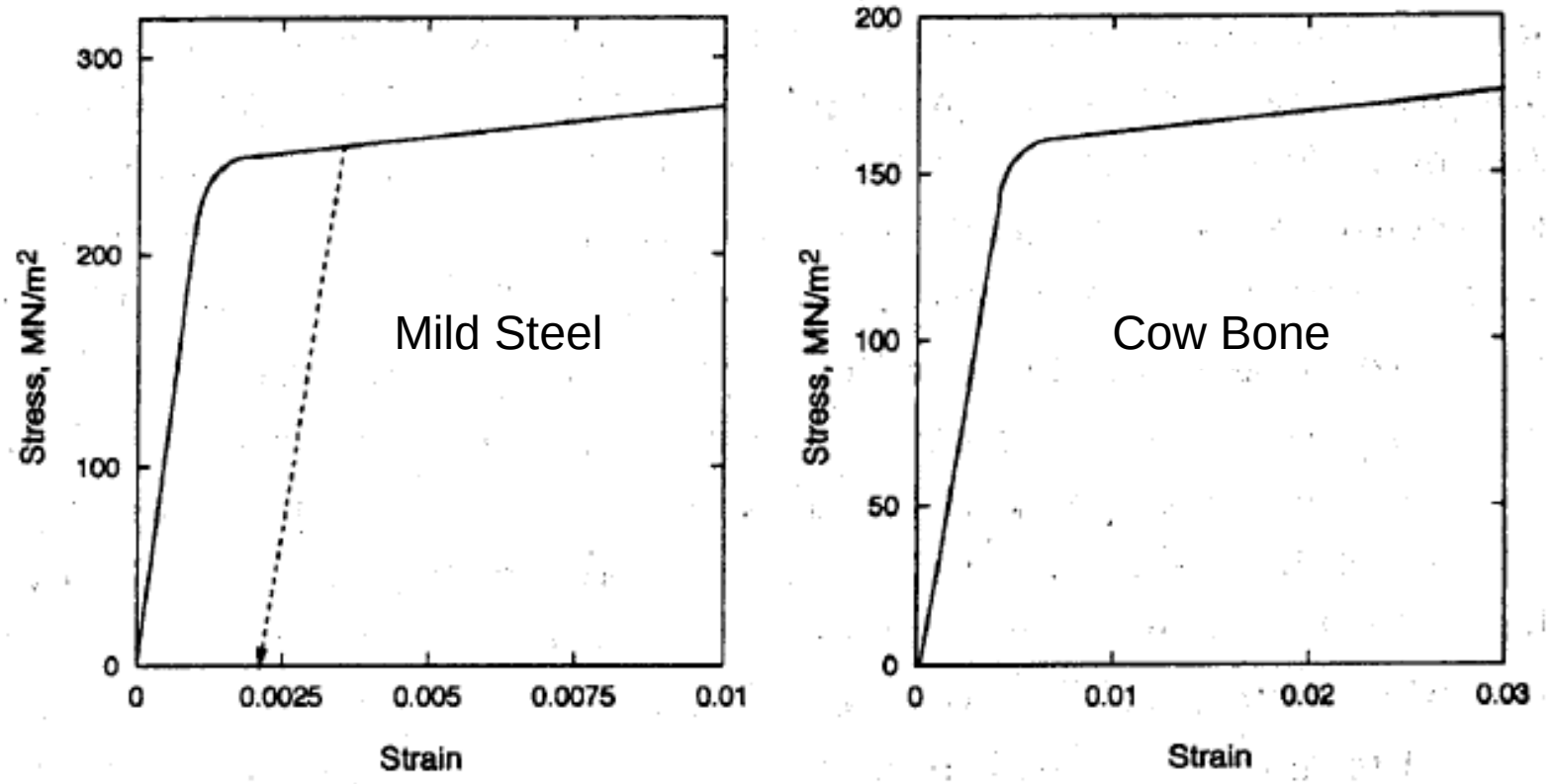


FIGURE 6.3. *Stress-strain curves for mild steel and for cow bone (data from Currey, 1984).*

7. Bioceramics

7.1 Types of biominerals

- Calcium carbonate: sea shells, calcifying algae
- Calcium phosphate (hydroxyapatite): vertebrate bone and teeth
- Silica: marine sponges, diatoms, some plants
- Iron oxides: limpets, chitons, bacteria
- Others: gypsum, strontium sulfate, barium sulfate, etc. etc.

$\rightarrow$ about 70 different biominerals

7. Bioceramics

Examples of most common biominerals

Mineral	Formula	Organism/Function
Calcite	$CaCO_3$	Algae/exoskeleton
Aragonite	$CaCO_3$	Molluscs/exoskeleton
Vaterite	$CaCO_3$	Ascidians/spicules
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	Vertebrates/endoskeleton
Weddelite	$CaC_2O_4 \cdot 2H_2O$	Plants/Ca store
Gypsum	$CaSO_4$	Jellyfish larvae/gravity
Barite	$BaSO_4$	Algae/gravity device
Celestite	$SrSO_4$	Acantharia/cellular support
Silica(opaline)	$SiO_2 \cdot nH_2O$	Algae/exoskeleton
Magnetite	Fe_3O_4	Bacteria/magnetotaxis Chitons/teeth
Goethite	α-FeOOH	Limpets/teeth
Lepidocrocite	γ-FeOOH	Limpets, chitons/teeth
Ferrihydrite	$5Fe_2O_3 \cdot 9H_2O$	Many organisms/Fe store
Greigite	Fe_3S_4	Bacteria/magnetotaxis

From: J. Webb et al. (1999). *Coord. Chem. Rev.* **190-192**, 1199-1215.

7. Bioceramics

Calcium Carbonate – $CaCO_3$

Most common biomineral in mollusks and many marine organisms

Exists in 3 different polymorphs (same composition, different crystal structure):

1. **Calcite:** trigonal - hexagonal scalenohedral

2. **Aragonite:** orthorhombic – dipyramidal

3. **Vaterite:** hexagonal

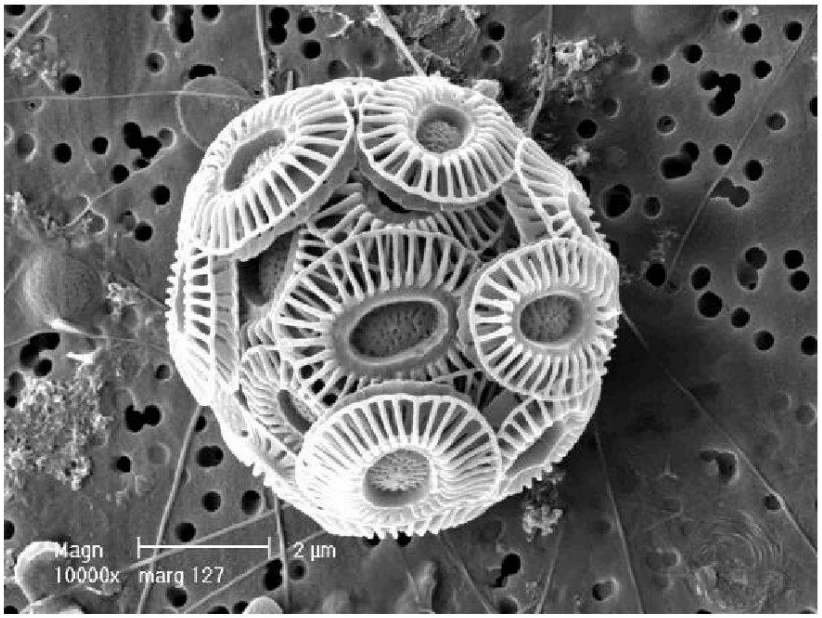
All of them colorless, transparent.

7. Bioceramics

Example of calcite mineralization

Calcifying algae - coccolithophores

Emiliania huxleyi



Emiliania huxleyi, © Jeremy R. Young,
Palaeontology Department, The Natural History Museum, London.

make: 1.5 mio tons of $CaCO_3$ per year
(predominant $CaCO_3$ production on earth)

Calcareous rocks

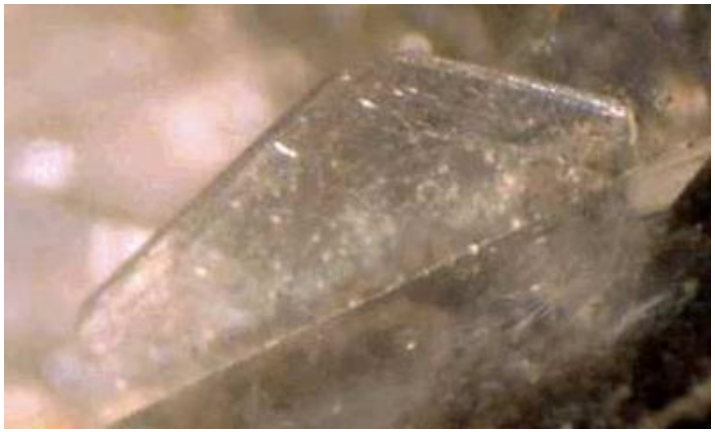
7. Bioceramics

Calcium phosphate

Mainly occuring as hydroxy apatite, $Ca_{10}(PO_4)_6(OH)_2$, hexagonal – dipyramidal

Colorless, transparent.

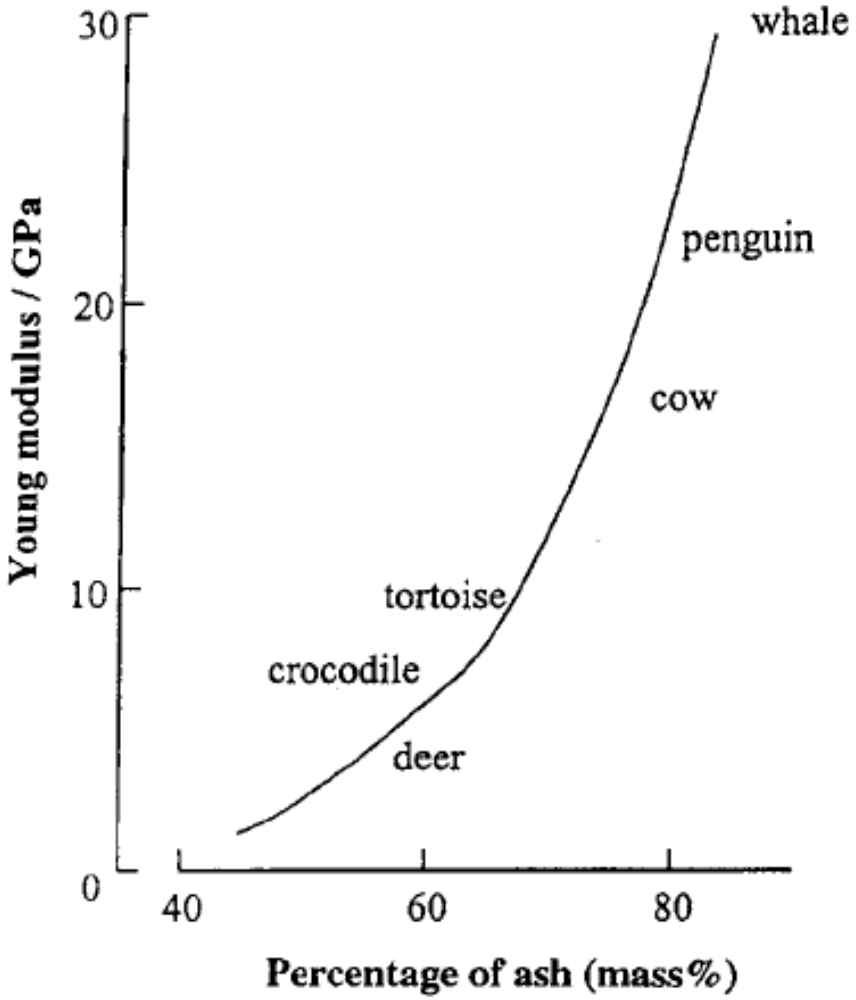
Mineral found in the hard parts of vertebrates (e.g. bones, teeth, fish scales)



7. Bioceramics

Degree of mineralization (amount of HAP) in bones

Increase in stiffness with increasing mineral content (mass %) for various cortical bones



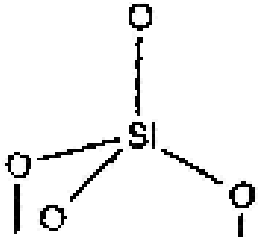
7. Bioceramics

Silica – SiO_2

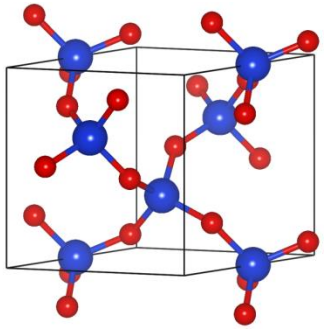
Crystalline SiO_2: quartz

most abundant mineral on earth, most sand is quartz sand

Trigonal – trapezohedral

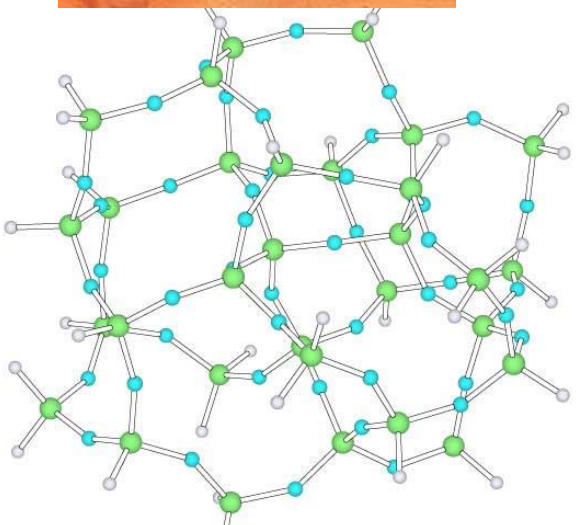


Crystal structure



Amorphous SiO_2: silica glass

Biogenic SiO_2 is amorphous!



Structure of silica glass

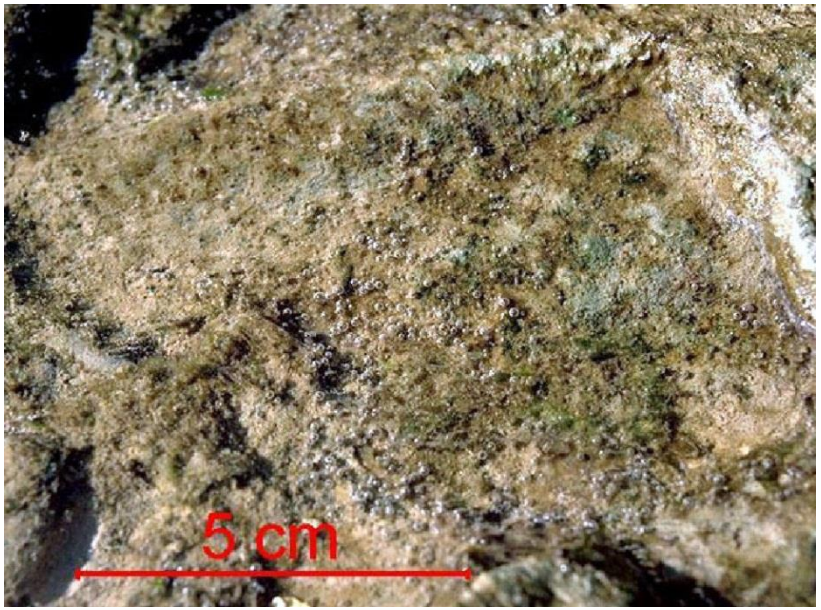
7. Bioceramics

Silica biomineralization

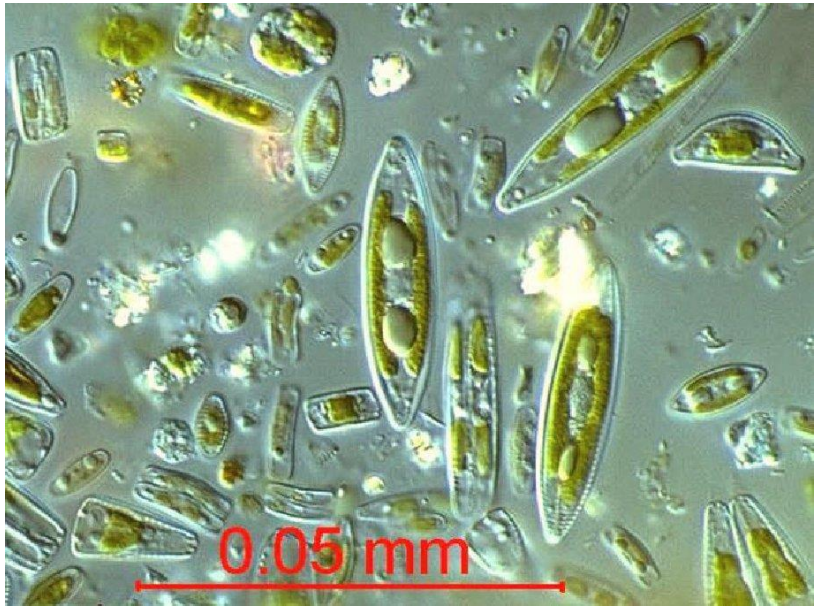
Example: **Diatoms**

Unicellular algae with mineralized cell walls (frustules) made from hydrated silica.

Macroscopic appearance: green slime (plankton)



Under the light microscope:

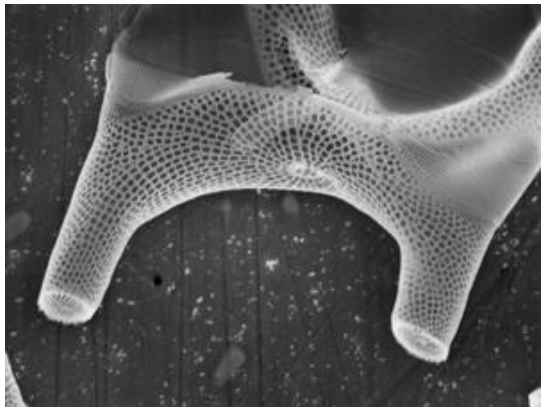


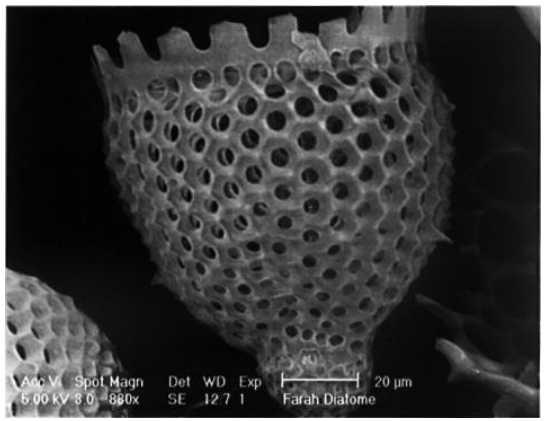
7. Bioceramics

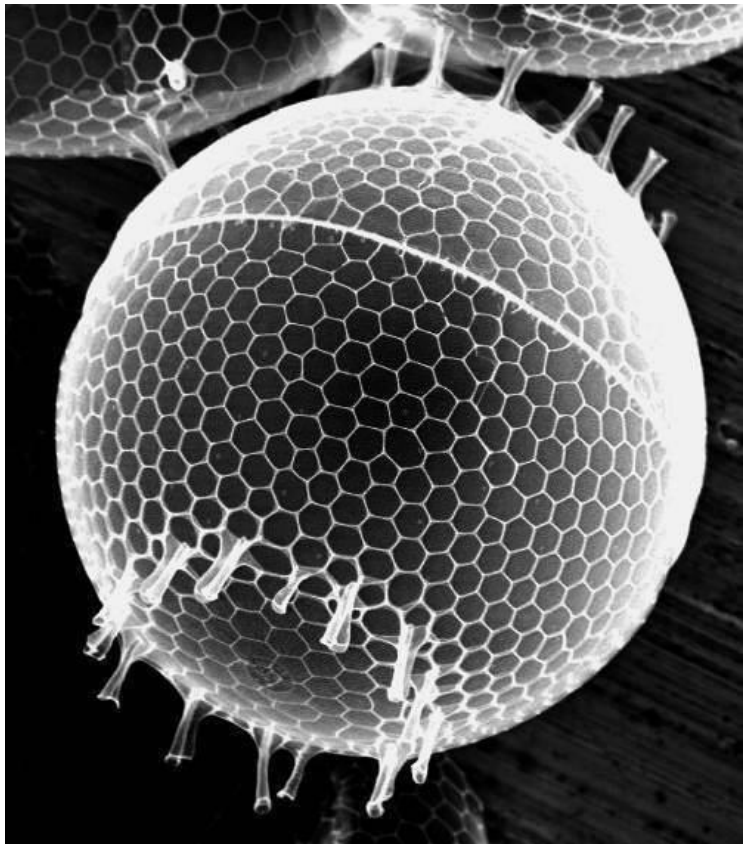
Silica diatom frustules

Occur in various shapes, depending on species. Complicated porous structures. Served as model for architecture of the entrance to World Exposition in Paris.

Scanning electron micrographs:



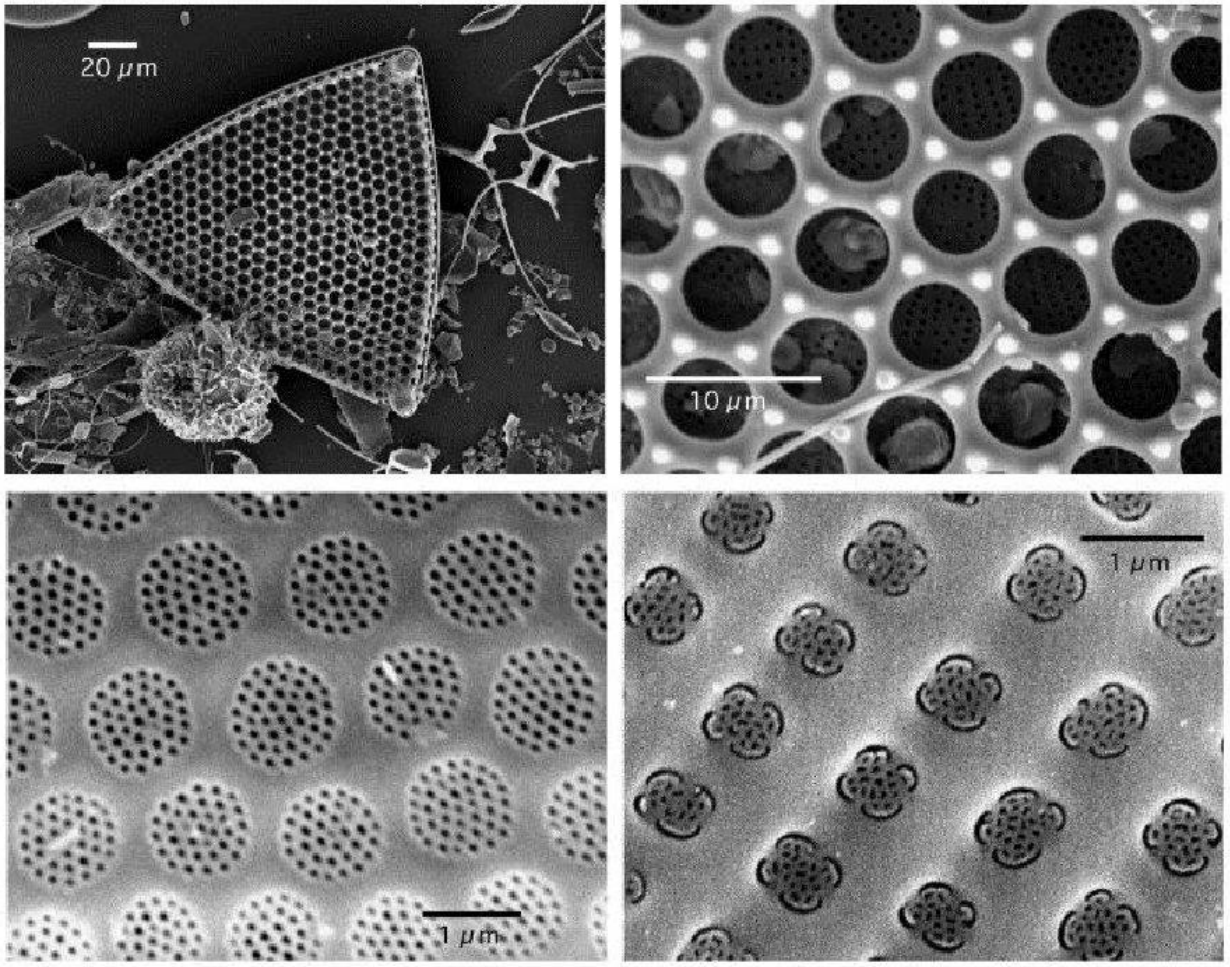




7. Bioceramics

Sieve structure of diatom frustules

Intricate porous patterns allow fluid exchange. Pore pattern is specific to species.



7. Bioceramics

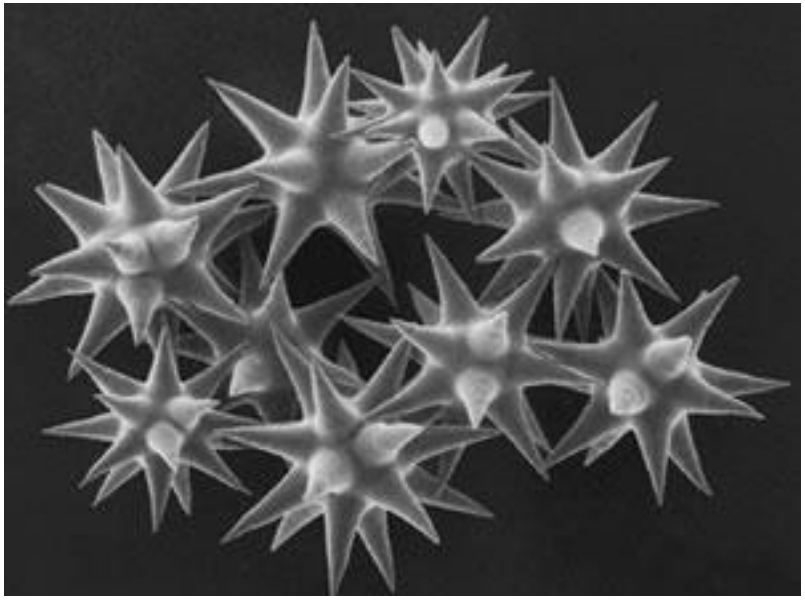
Silica in marine sponges

Marine sponge *Tethya aurantia*.

Protein group silicateils were found catalyze silica skeletal formation from silicic acid, the form in which silicon enters the sponge.

Photo of *Tethya aurantia*

SEM image of silica structures in *Tethya aurantia*

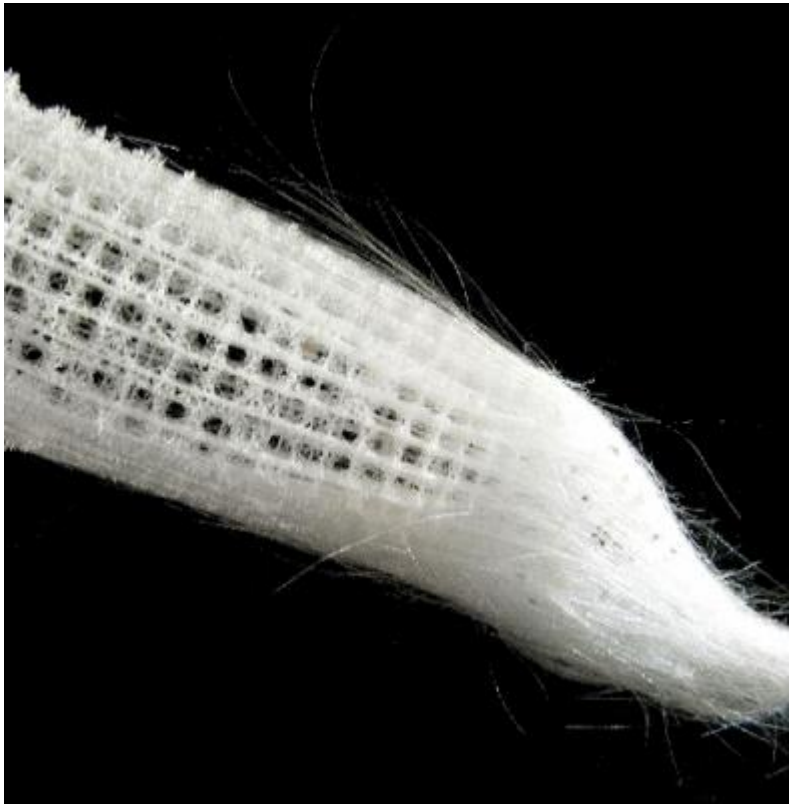


7. Bioceramics

Marine sponge Euplectella

„Venus basket“, consists of silica fibers, built in concentric layers around a hollow interior filled with protein.

Concentric construction and protein makes fibers much less brittle than glass would normally be.



7. Bioceramics

Silica from plants

Plants mostly contain little to no mineral.

Silica occurs in some grasses (defence against grazing animals)

Equisetum (Horsetail):

Up to 10 % wt silica, abrasive stems.

Very old species (“living fossil”)

Uses by humans: scour pans (tin), polish wood, tooth cleaning

Equisetum arvense (common Horsetail)

7. Bioceramics

Iron minerals

Magnetite Fe_3O_4: Magnetite particles in bacteria, honey bees, bird brains... etc., teeth of chiton (marine mollusc)

Lepidocrocite β-FeOOH: in teeth of chiton (marine mollusc)

Goethite α-FeOOH: radula teeth of limpets (marine mollusc)

7. Bioceramics

Other minerals

Gypsum: $CaSO_4.2H_2O$, as gravity receptor in jellyfisch

Celestite: $SrSO_4$, micro-skeleton of acantharia (20 spines, each is a single crystal, a axis parallel to the morphological longitudinal axis

Barite: $BaSO_4$, mineral with high specific gravity, gravity receptor (intracellular crystallites) in desmids (unicellular algae)

Acantharia: celestite

Desmids: barite

7. Bioceramics

What is special about BIO-mineralization?

- uniform particle sizes
- well-defined structures and compositions
- high levels of spatial organization
- complex morphologies
- controlled aggregation and texture
- preferential crystallographic orientation
- higher-order assembly into hierarchical structures

7. Bioceramics

7.2 Control mechanisms in biomineralization

1. **Chemical:** the thermodynamic conditions for precipitation of mineral from solution is strictly controlled. Chemical conditions (e.g. pH, temperature) determine solubility and supersaturation.
2. **Structural:** mineral structure is determined by organic template. Interfacial molecular recognition causes selected crystallographic orientation or specific crystal structure (polymorph).
3. **Morphological:** control of shape by controlled deposition of the mineral and selective growth inhibition
4. **Spatial:** mineralization is confined to vesicle or porous organic framework (supramolecular preorganization of organic molecules)

7. Bioceramics

Ad 1) Chemical control: amorphous - crystalline

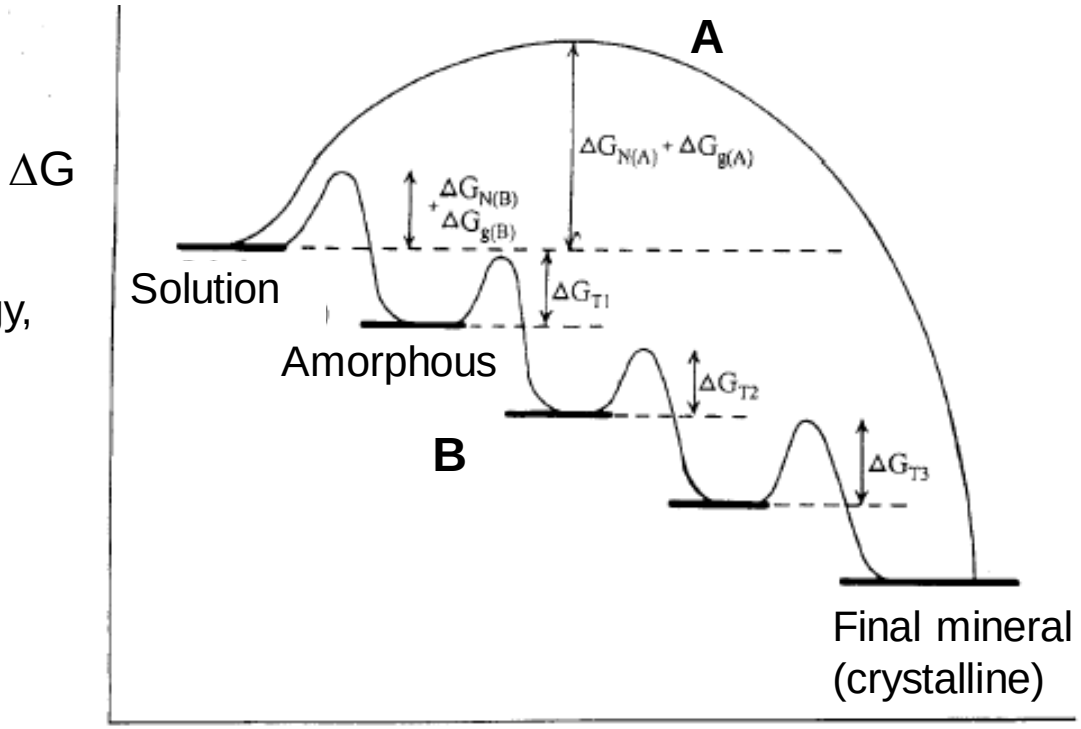
Amorphous phases are more soluble than their crystalline counterparts.

Biomineralization:

often starts with amorphous granules (sometimes formed far from crystallization site and transported to the organic matrix where they form minerals).

Crystallization: via a number of steps (path **B**) instead of one large step (path **A**).

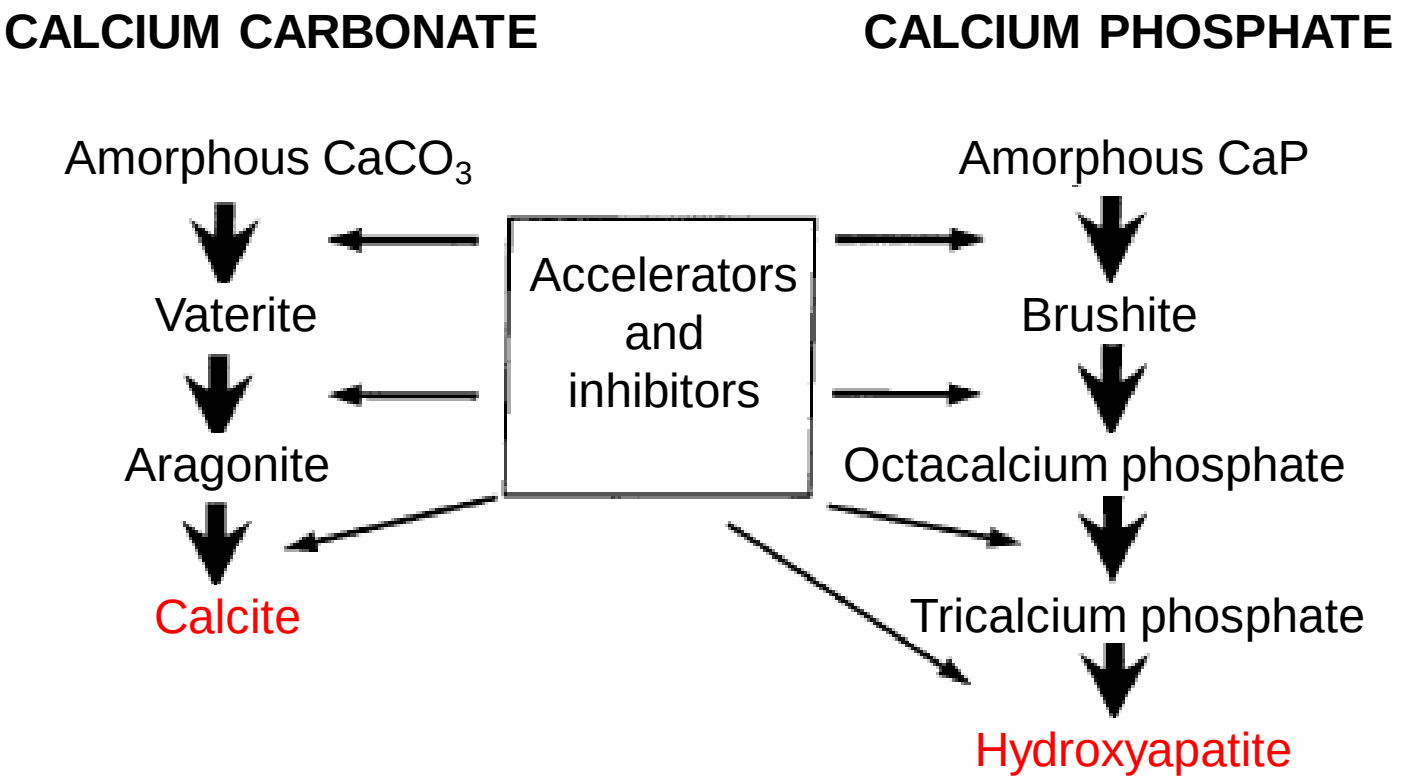
G: Gibbs energy, free enthalpy



7. Bioceramics

Chemical control: amorphous - crystalline

Step-wise crystallization in calcium carbonate and calcium phosphate:



Amorphous calcium phosphate slowly turns into HAP crystals at RT in aqueous media (same with $CaCO_3$: turns into calcite), only silica stays amorphous (activation energy for transformation into quartz is very high)

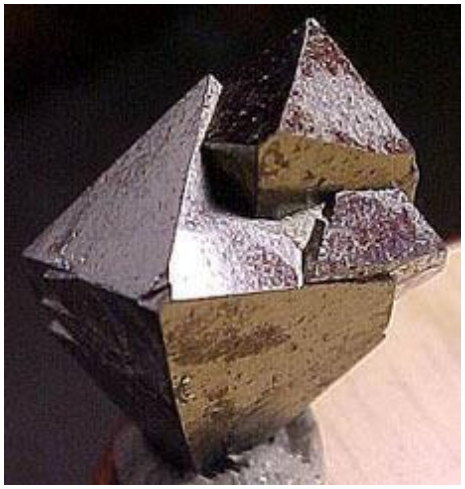
7. Bioceramics

Example of chemical control: from rust to magnetite

Special example of chemically controlled mineral formation

Production of magnetite at physiological temperatures (magnetotactic bacteria, chitons, limpets): transformation of ferrihydrite (rust) into magnetite: will not happen spontaneously!

rust: ferrihydrite Fe_2O_3 . n H_2O



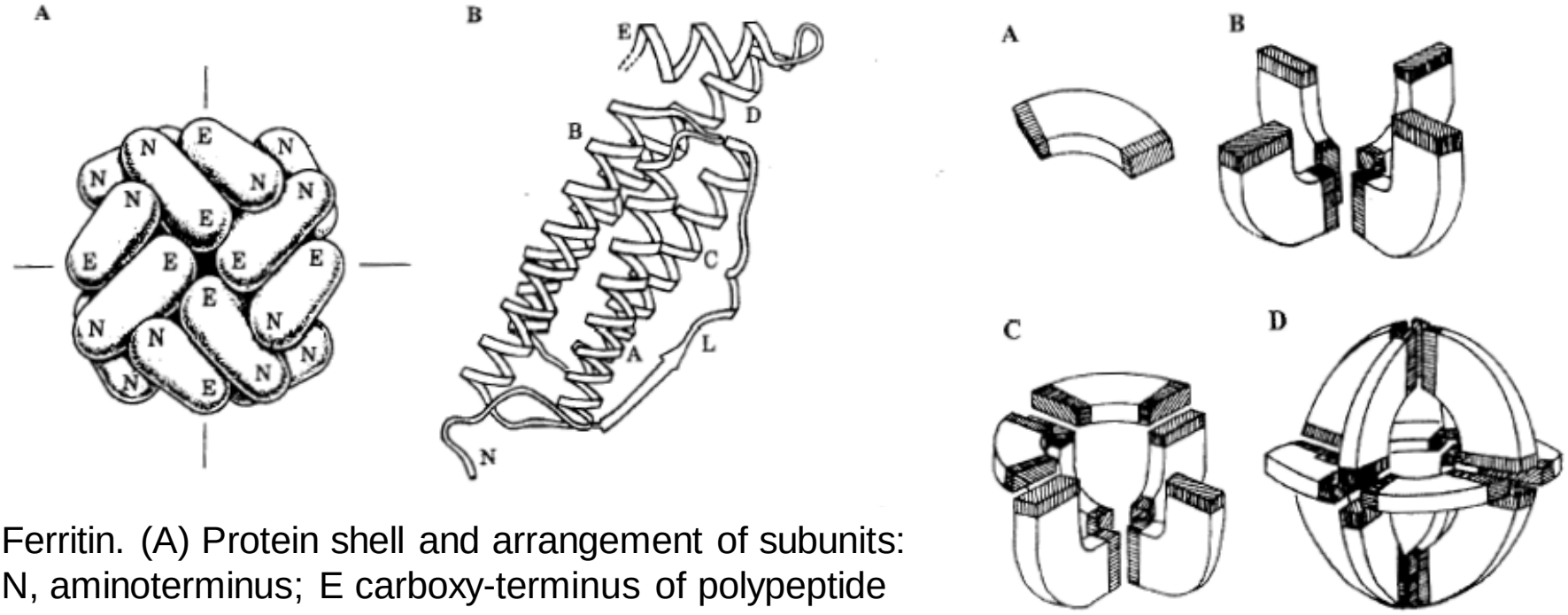
Magnetite Fe_3O_4

7. Bioceramics

Iron storage protein ferritin

Ferritin protein shell (8 hydrophilic and 6 hydrophobic pores, core: ferrihydrite). Also present in human body. Provides safe (non-toxic) iron storage.

Important role in iron storage and transport also in magnetite forming organisms.



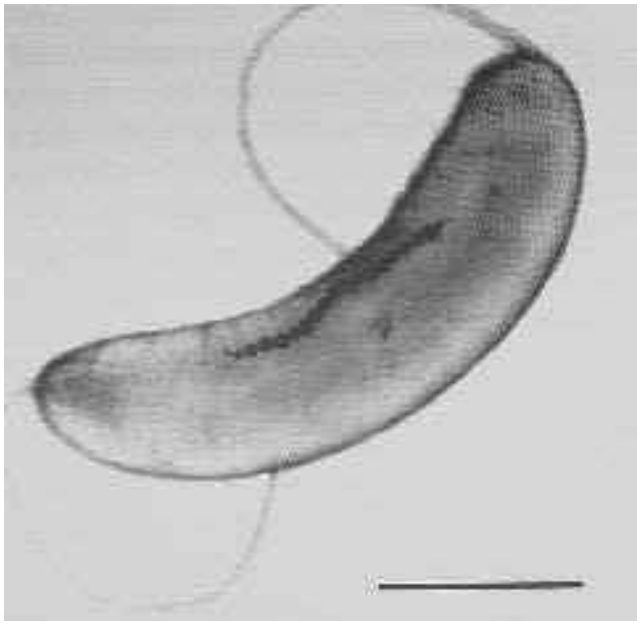
Ferritin. (A) Protein shell and arrangement of subunits: N, aminoterminus; E carboxy-terminus of polypeptide chain. (B) Single subunit showing bundle of four alpha-helical domains (A-D), loop region (L) and small helix (E) of the polypeptide chain.

7. Bioceramics

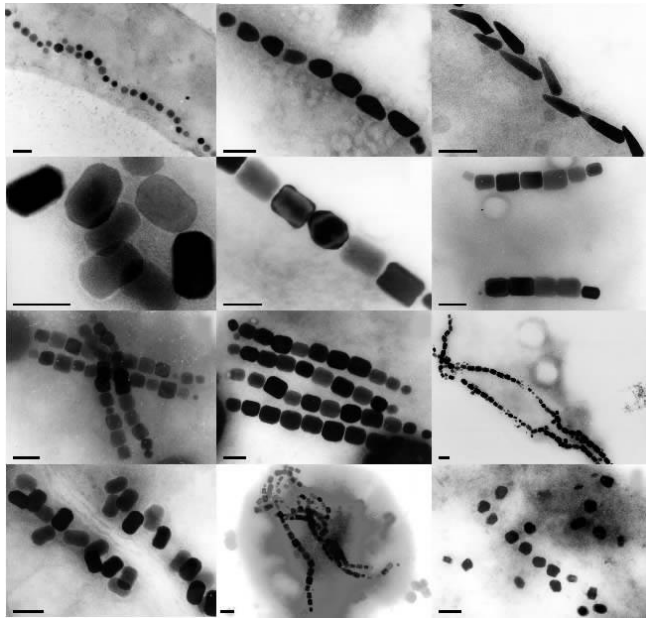
Magnetotactic bacteria

Contain magnetite particles (magnetosome particles) aligned in chains.

Exact shape and arangement depends on species (see images on the right). Particles always aligned in chains.



Magnetotactic bacterium



Magnetite particles in various species

7. Bioceramics

Magnetite biomineralization

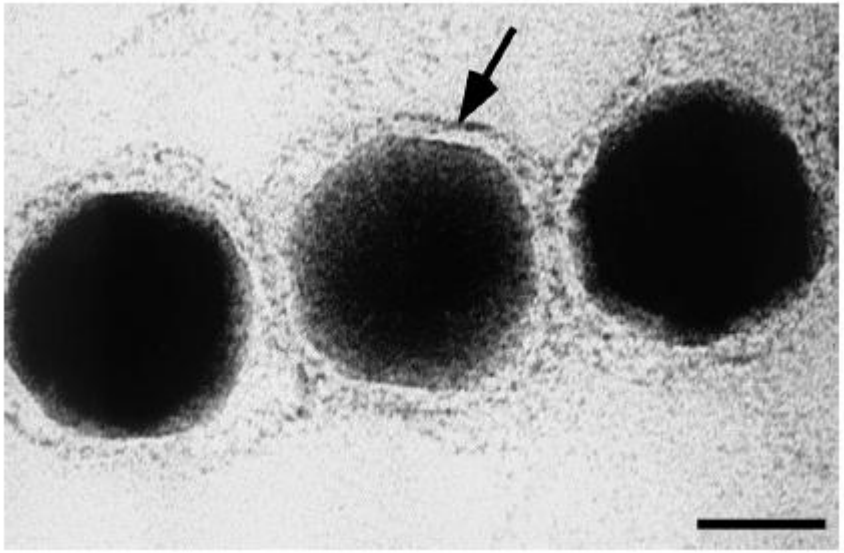
Phase tranformation ferrihydrite-magnetite happens inside of phospholipid vesicles, strict control over redox conditions and pH is necessary to reduce a third of the FeIII ions to FeII, as they are found in magnetite

Steps involved

- solid state transformation into hematite Fe_2O3
- dissolution and slow reprecipitation: goethite FeOOH
- reductive dissolution: magnetite Fe_3O_4

7. Bioceramics

Magnetite particles



Magentosome particles isolated from *Magnetospirillum gryphiswaldense.*

The magnetite crystals are typically 42 nm in diameter and are surrounded by the magentosome membrane, which prevents agglomeration (scale bar: 25 nm).

D. Schüler and R.B. Frankel (1999). Bacterial magnetosomes: microbiology, biomineralization and biotechnological applications. Applied Microbiology and Biotechnology 52 (4), 464-473.

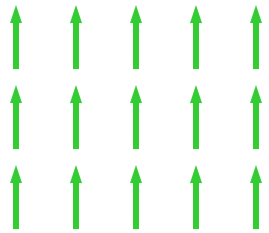
7. Bioceramics

Magnetism

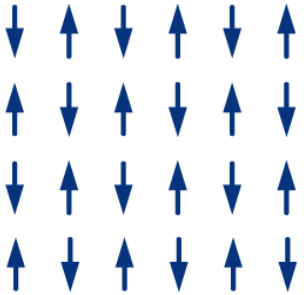
Magnetism is caused by orientation of atomic spins in material.

3 possibilities of permanent magnetism (without external magnetic field):

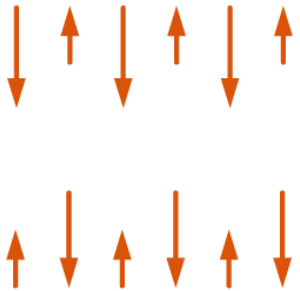
ferromagnetic



antiferromagnetic



ferrimagnetic



Magnetite is ferromagnetic!

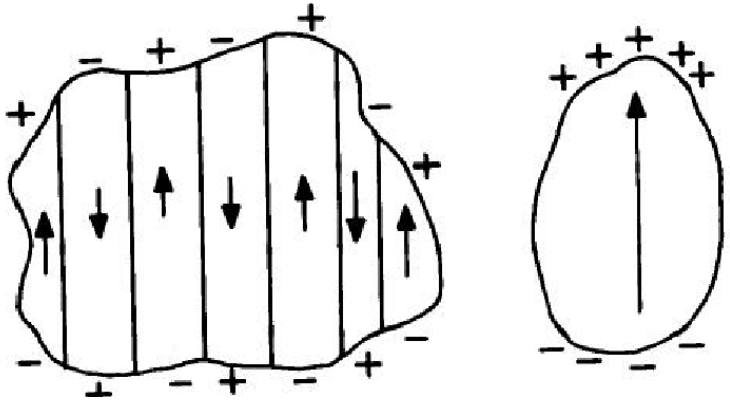
7. Bioceramics

Size of magnetic particles

Magnetic material consists of magnetic domains. Magnetic moments of different domains not necessarily oriented in same direction.

Reduction of size can lead to single domain particle (maximum magnetic moment for given particle size).

If size is further reduced, particle becomes paramagnetic (spins flip randomly).

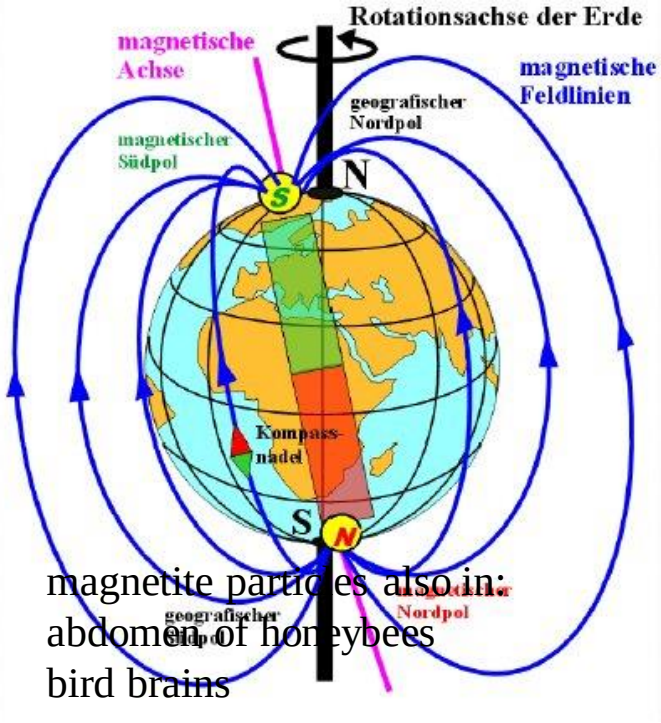


Magnetite particles in magnetotactic bacteria are single domain particles! Strict control over size and shape (particle size between 40-100 nm).

Size is so special that magnetite particles have been looked for in the Martian meteorites as a possible sign of extraterrestrial life

7. Bioceramics

Orientation with magnetic particles



magnetite particles also in:
abdomen of honeybees
bird brains

Magnetotaxis

A widely accepted hypothesis about the function of magnetotaxis is that, because all known magnetotactic bacteria are either microaerophilic or anaerobic, they seek to avoid high oxygen levels and their navigation along the geomagnetic field lines facilitates migration to their favored position in the oxygen gradient (Frankel and Bazylinski 1994). The preferred motility direction found in natural populations of magnetotactic bacteria is northward in the geomagnetic field in the northern hemisphere, whereas it is southward in the southern hemisphere. Because of the inclination of the geomagnetic field, migration in these preferred directions would cause cells in both hemispheres to swim downward.

D. Schüler and R.B. Frankel (1999). Bacterial magnetosomes: microbiology, biomineralization and biotechnological applications. Applied Microbiology and Biotechnology 52 (4), 464-473.

7. Bioceramics

Ad 2) Structural control

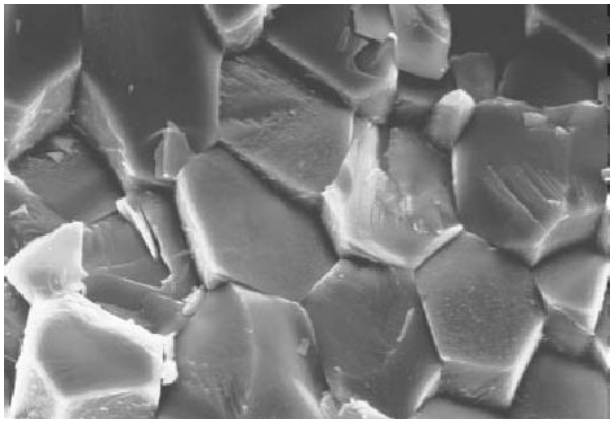
Influence on the crystalline structure of the biomineral by organic templates. Interfacial molecular recognition causes selected crystallographic orientation or specific crystal structure (polymorph).

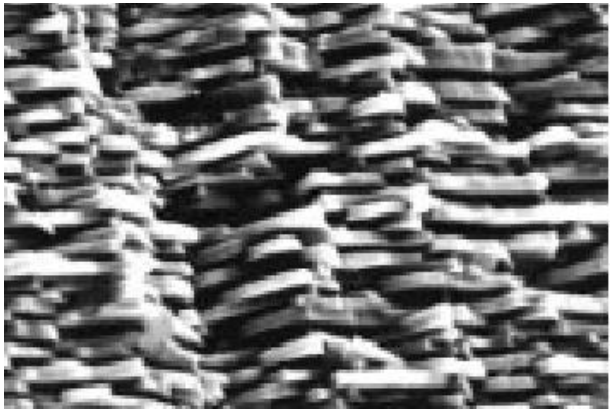
(a) Influence on the polymorph

(b) Influence on crystal orientation

7. Bioceramics

(a) Control of polymorph: aragonite platelets in nacre



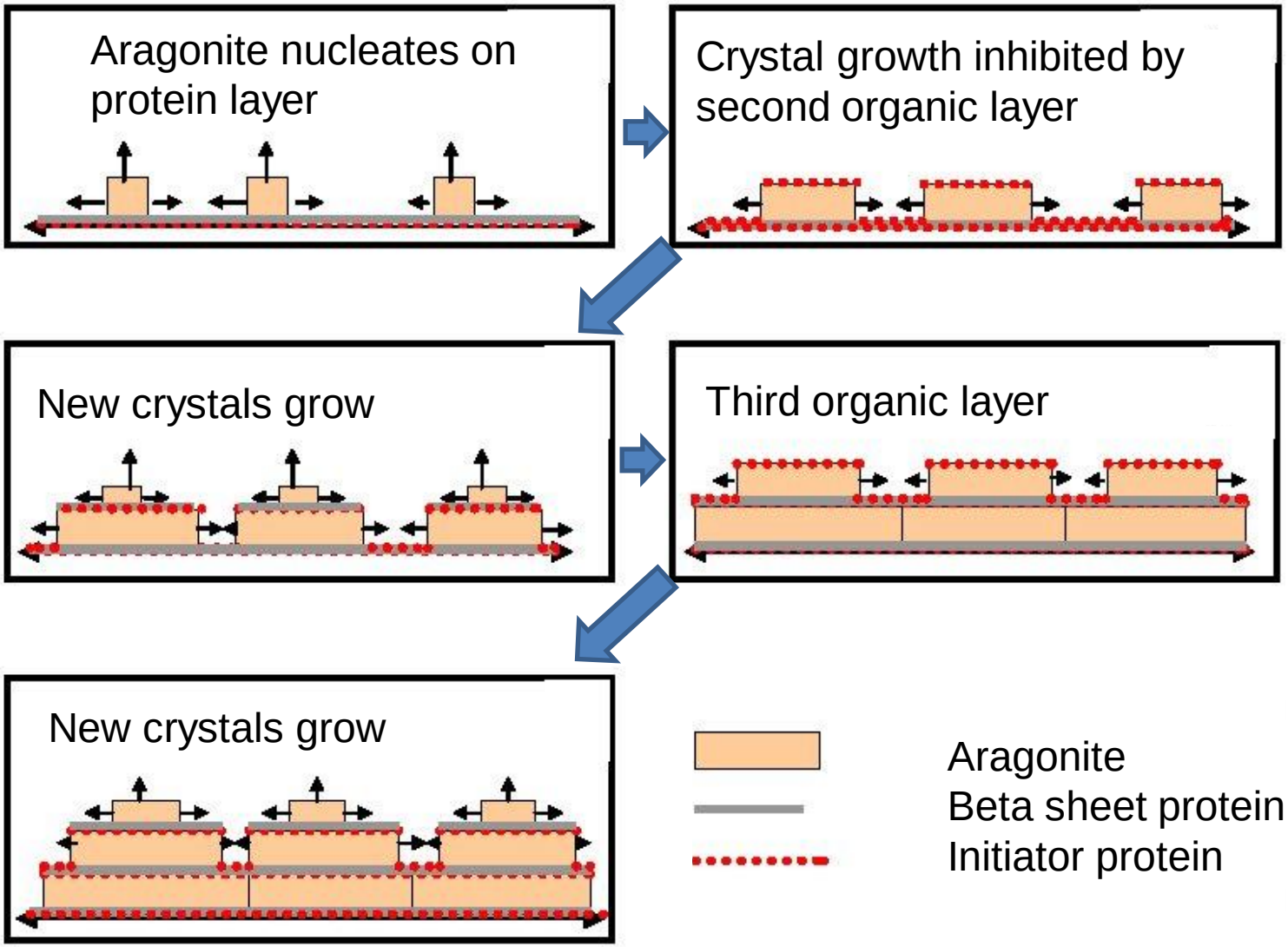


Aragonite: metastable form of $CaCO_3$ (calcium carbonate)

Sequence of polymorphs with increasing stability: vaterite $\rightarrow$ aragonite $\rightarrow$ calcite

7. Bioceramics

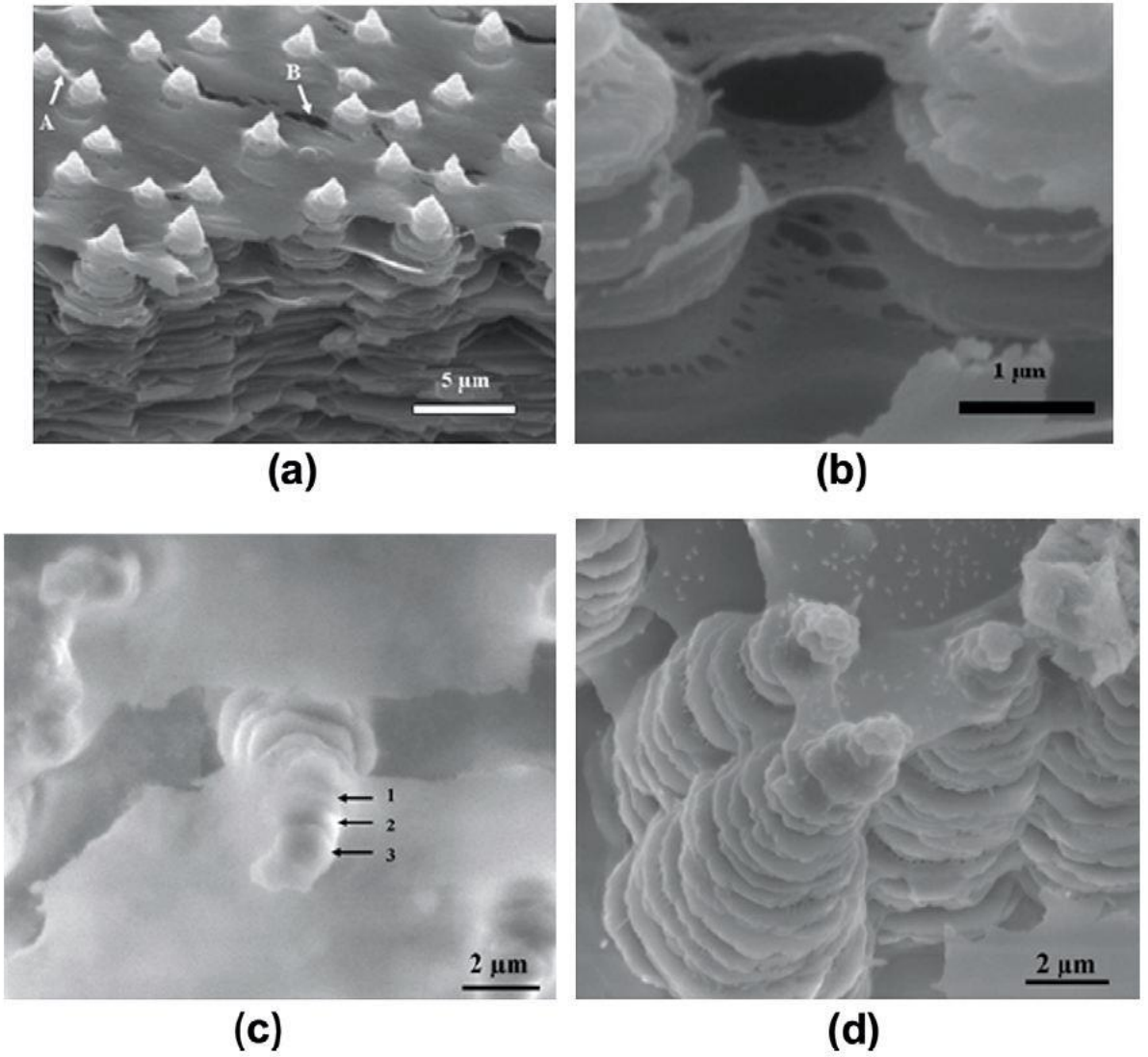
Model of controlled growth of aragonite in nacre



7. Bioceramics

Growth of aragonite

SEM images



Meyers MA, et al. Mater Sci Eng C, 2010; 29:2398–410.

7. Bioceramics

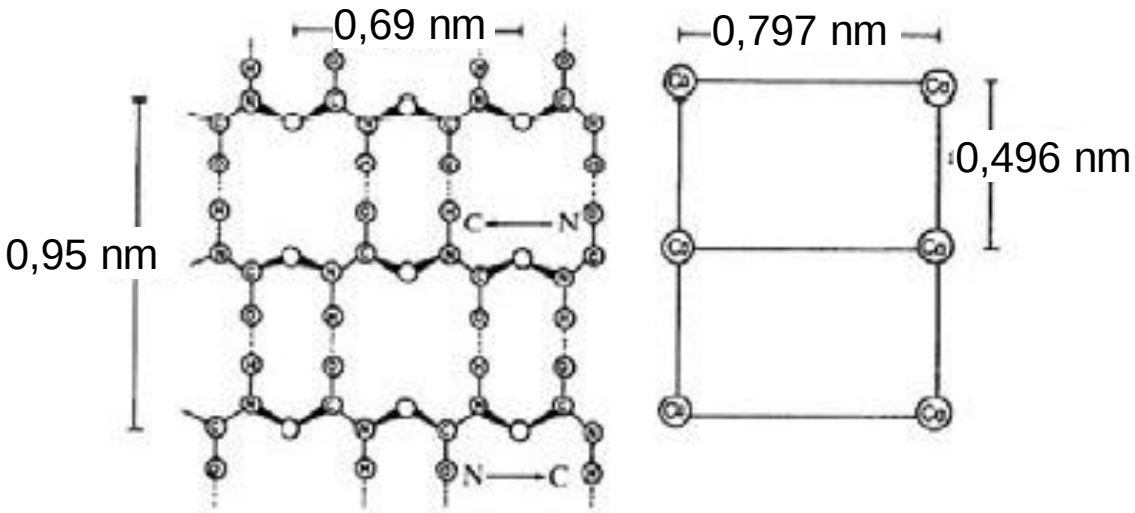
Nucleation of aragonite – molecular recognition

Nucleation of aragonite (metastable form of calcium carbonate) instead of calcite (stable form).

Likely reason: structure of organic layer between platelets.

Consider inter-atomic spacings:

β-sheet protein



Spacings in aragonite a-b-plane

Better match can be achieved with aragonite instead of calcite!

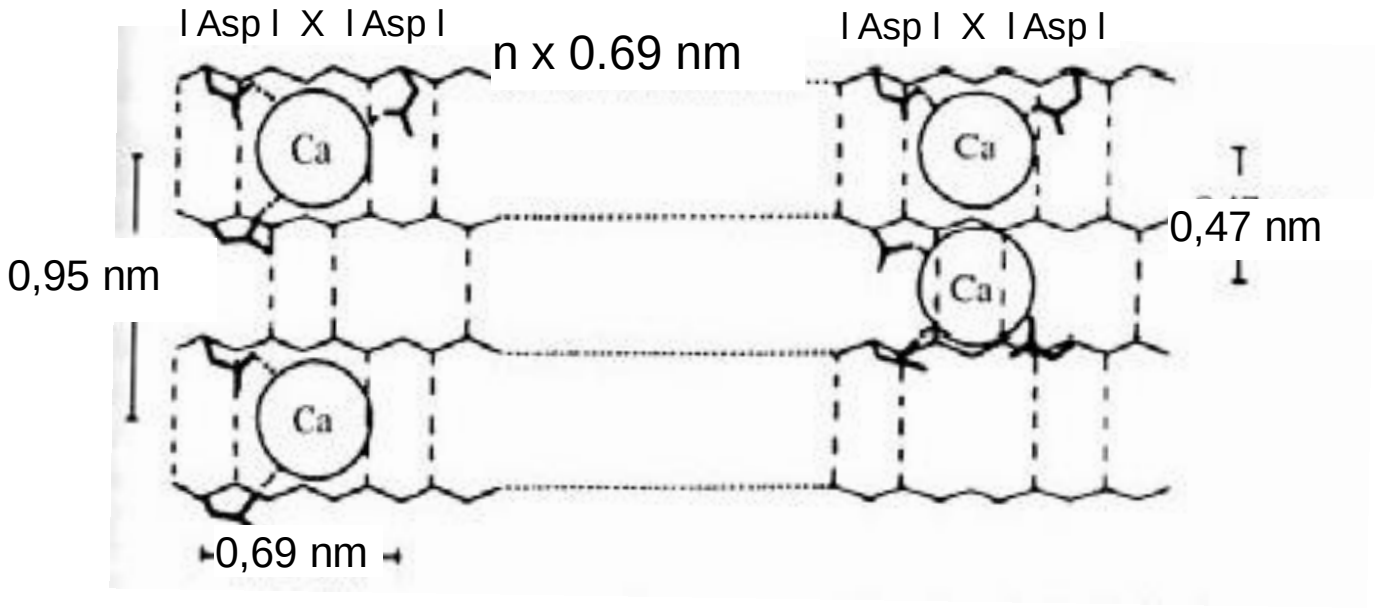
From: S. Mann, Biomineralization, Oxford University Press 2001.

7. Bioceramics

Nucleation of aragonite – molecular recognition

β-sheet protein is covered with acidic nucleation layer, rich in aspartate (Asp). Geometry of underlying b sheet is assumed to be preserved.

Model for geometric match of acidic protein and Ca-ions in aragonite:



Consequence: aragonite in nacre is stable! (stabilized by organic layer), does not turn into calcite.

From: S. Mann, Biomineralization, Oxford University Press 2001.

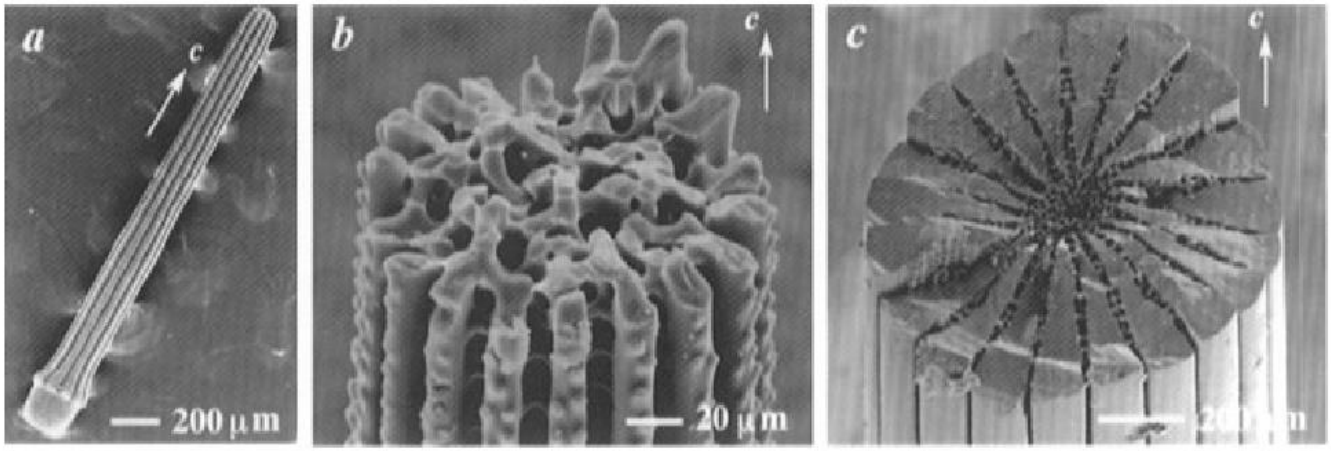
7. Bioceramics

(b) Control of crystal orientation

Example: Calcium carbonate ($CaCO_3$) in sea urchin spines

Sea urchin spines: mineralized spines, diffract like single crystals

But: consist of crystallites all oriented in the same direction, with very little protein (0.5 % wt) as thin layer laid down on growing surface → strength and stiffness of ceramics at reduced brittleness



Scanning electron micrographs of secondary spines from the sea urchin Paracnetrotus lividus. The direction of the c axis of the calcite crystal is indicated: (a) intact spine; (b) fracture surface of a young spine; (c) fracture surface of the mature spine.

7. Bioceramics

Crystal orientation in sea urchin spines

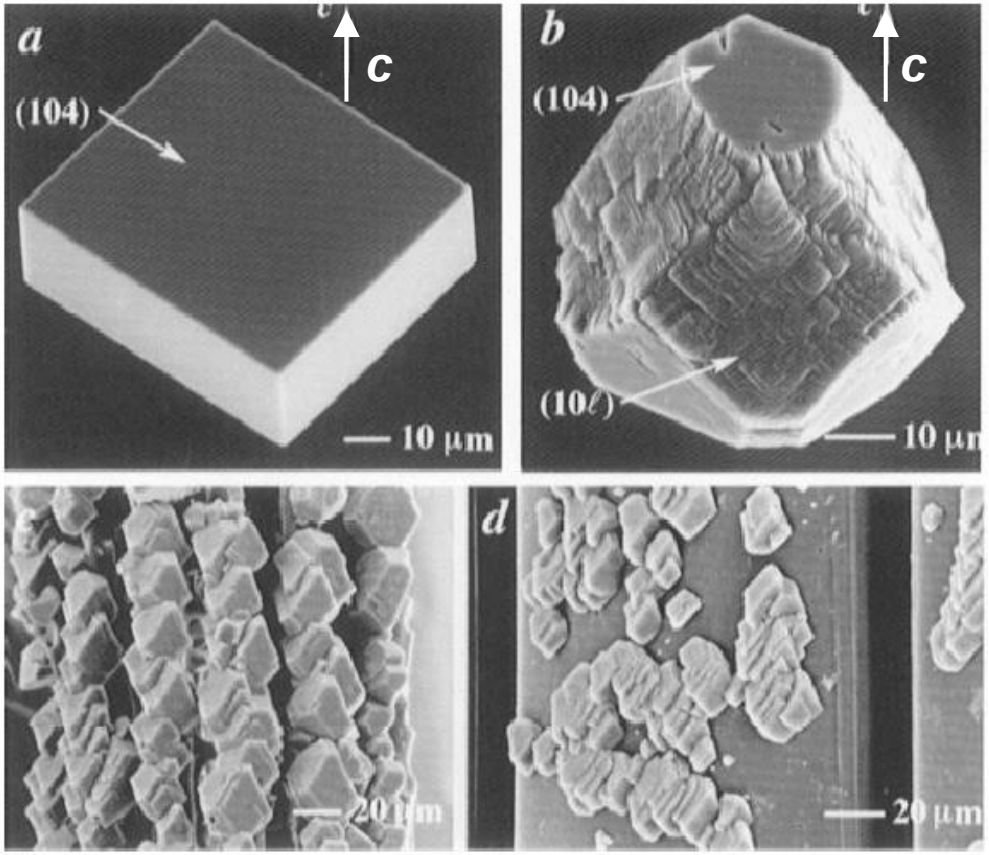
Experiment: precipitation of $CaCO_3$ in the laboratory.

(a) Pure synthetic calcite crystal grown in the absence of additives. Only the stable {104} hexagonal faces are expressed.

(b) Synthetic calcite crystal grown in the presence of the macromolecules extracted from P. lividus spines.

(c) New calcite crystals overgrown epitaxially on the lateral surface of a young spine. Note that the same faces as in (b) are developed.

(d) New calcite crystals overgrown epitaxially on the lateral surface of the mature spine. The morphological effect is identical to that in (c).



c-axis indicated by arrow.

From: S. Mann, Biomineralization, Oxford University Press 2001.

7. Bioceramics

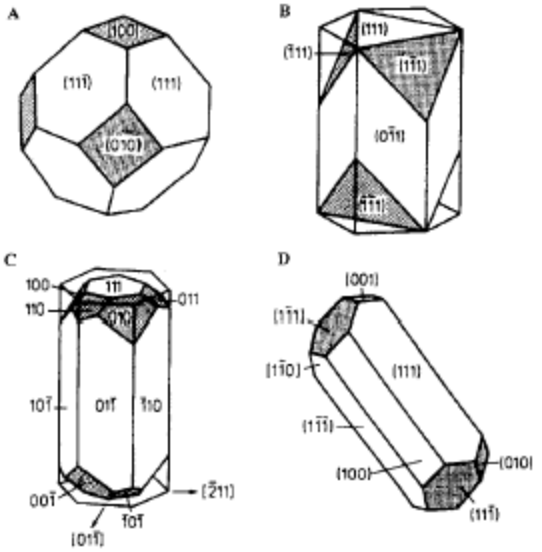
Ad 3) Morphological control

Control of exterior shape. Sometimes leads to apparent breaking of crystal symmetry.

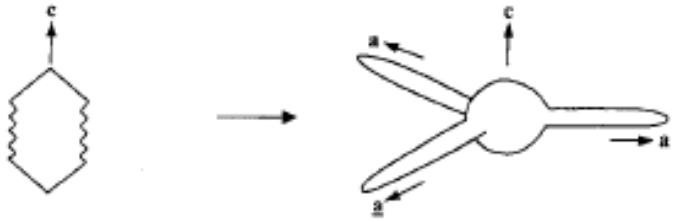
Biological macromolecules attach to specific crystal surfaces and inhibit growth in this direction.

Examples:

Morphological types of bacterial magnetite single crystals. (A) cubo-octahedron, (B) and (C) hexagonal prisms, and (D) elongated cubo-octahedral.



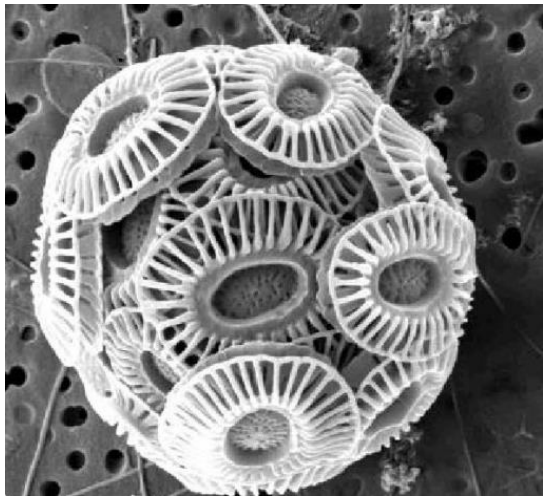
Development of larval sea urchin spicule (single calcite crystal!)

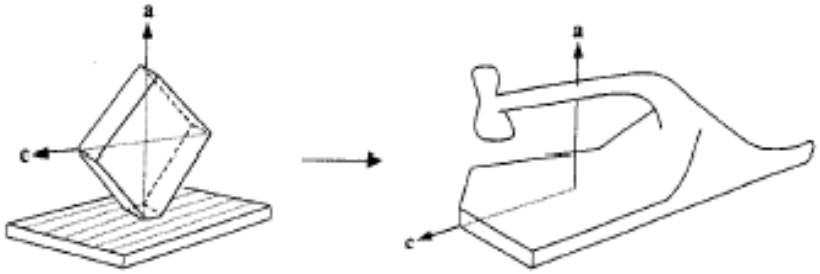


7. Bioceramics

Morphological control in coccolithophores

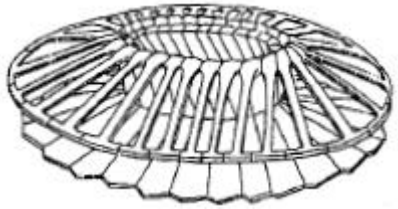
Coccolithophores: calcifying algae





Development of coccolith plate (single calcite crystal!)

From: S. Mann, 2001.



Drawing of coccolith based on an elliptical array of discrete structural units.

7. Bioceramics

Ad 4) Spatial control

Confinement of biomineralization in organic network.

Example: mineralized bone formation inside compartment formed by bone cells (osteoblasts)

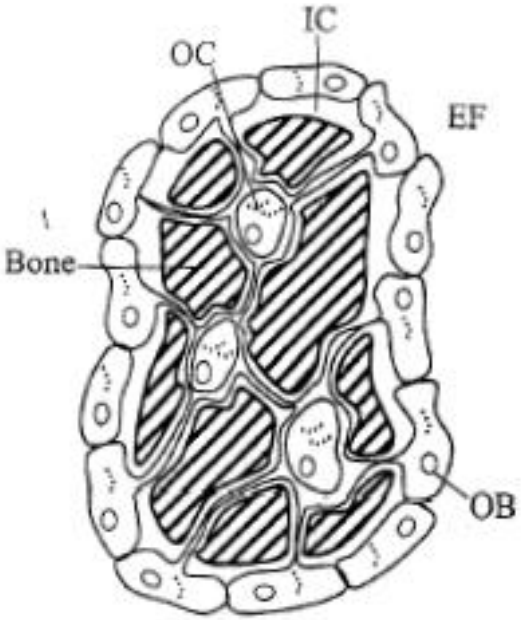


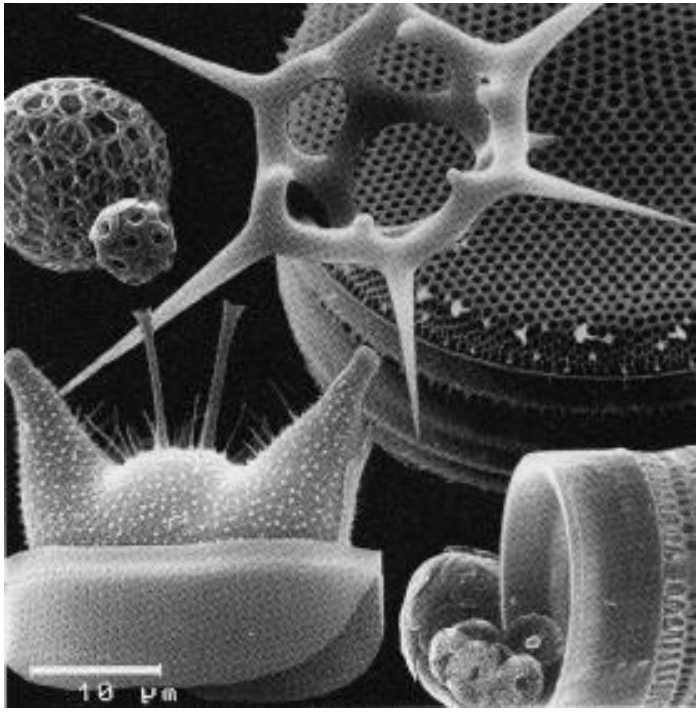
Fig. 5.13 Cellular assemblies in boundary-organized bone formation. IC, inner compartment; OB, osteoblasts; OC, osteocytes; EF, extracellular fluid.

From: S. Mann, 2001.

7. Bioceramics

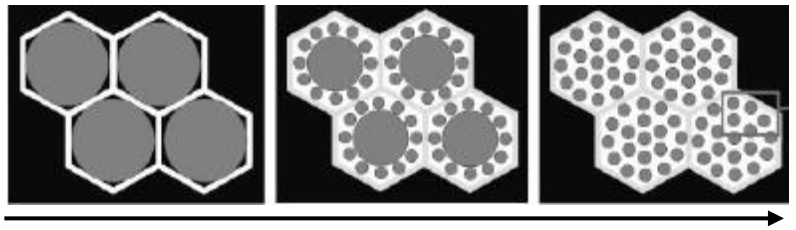
Spatial control in silica diatoms

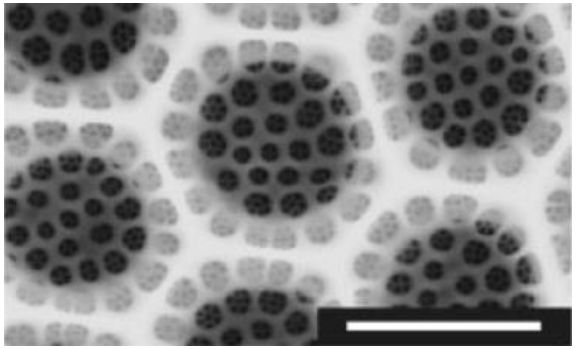
Formation of mineral outside compartment formed by temporary vesicles.



Different kinds of diatoms

Model of silica deposition around vesicles





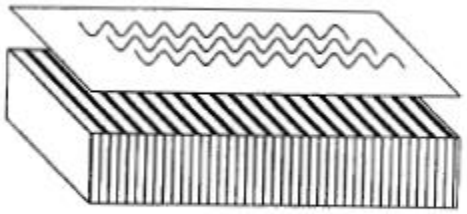
SEM image of *Coscinodiscus* shell

7. Bioceramics

Organic matrix mediated biomineralization

Interaction (compatibility) of organic matrix and nucleating mineral is required!

Organic matrix often highly cross-linked, hydrophobic material. Additional hydrophilic (often acidic) protein sheath for nucleation:



Two component model of the organic matrix

7. Bioceramics

Examples of framework + nucleating surface

System	Framework macromolecules	Acidic macromolecules
Bone and dentin	Collagen	• Glycoproteins: Osteopontin, Osteonectin • Proteoglycans: Chondroitin sulfate, Keratan sulfate
Tooth enamel	Amelogenin	• Glycoproteins: Enamelins
Mollusc shells (nacre)	β-Chitin, silk-like proteins, lustrin A	• Glycoproteins: Nacrein, N66
Crab cuticle	α–Chitin	• Gycoproteins: HEP200, Silaffins
Silica Sponges	Silicatein	No data
Plant silica	Cellulose	• Proteins • Carbohydrates (xylose, glucose)

7. Bioceramics

Summary: Principles of biomineralization

Controlled deposition:

1. **chemical:** amorphous/crystalline/crystalline polymorph: e.g. rust to magnetite in magnetic bacteria
2. **structural**: control of crystal polymorph in nacre (aragonite instead of calcite), strict orientation of $CaCO_3$ in sea urchin spine
3. **morphological**: e.g. sea urchin larval spicules, coccoliths
4. **spatial control**: bone formation in osteocyte vesicle

Matrix mediated biomineralization:

biomineral deposition on structural framework, e.g. tooth enamel

7. Bioceramics

7.3 Examples of biomineralized tissues

7.3.1 Nacre (mother of pearl)

7.3.2 Minerals for optics: calcitic lenses

7.3.4 Calcified vertebrate teeth

7.3.5 Metal based worm teeth

7. Bioceramics

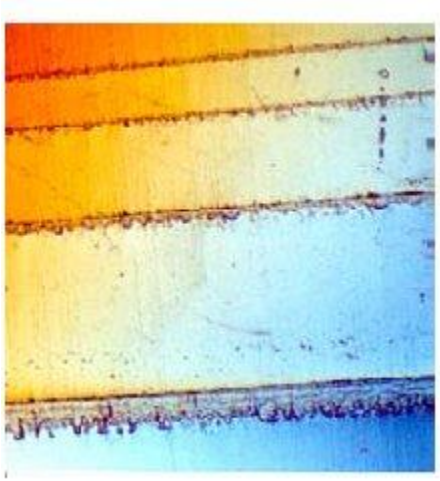
7.3.1 Nacre – mother of pearl

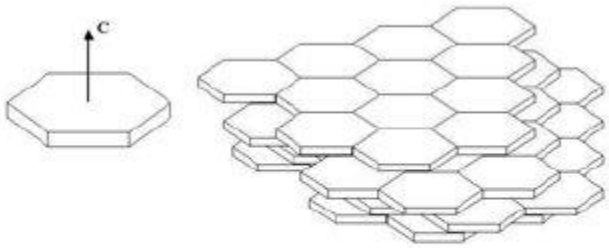
Inner part of see shells

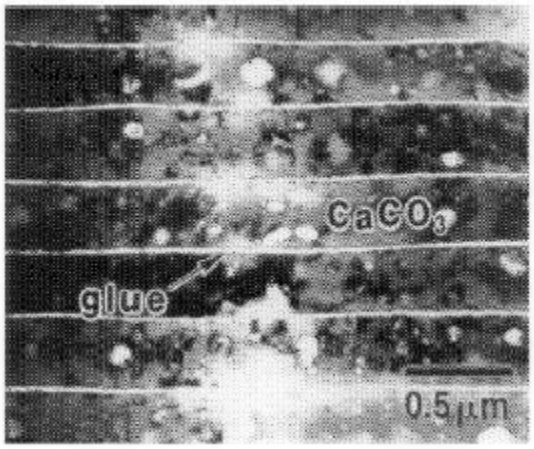
Consists of aragonite (metastable $CaCO_3$ polymorph) platelets + thin organic layer approx. 1 % wt.)

Thickness of platelets: 300 nm - 1 micrometer (close to wavelength of visible light, typical iridescence)

e.g. Strombus gigas





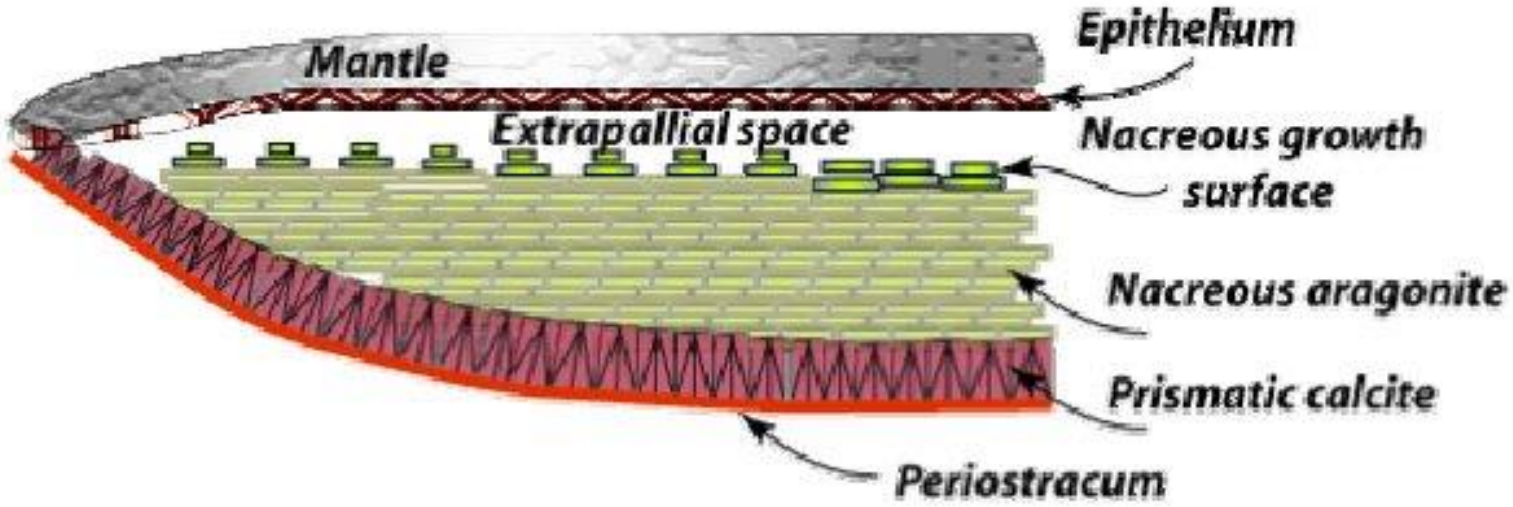


7. Bioceramics

Abalone shell

Halilotis rufescens (red abalone), large shell with thick nacreous layer.

Popular system for studies on nacre.



7. Bioceramics

Remember: $CaCO_3$ in nacre is aragonite, not calcite

$CaCO_3$ is forced to nucleate as metastable polymorph aragonite, due to geometry in protein sheet.

Aragonite in nacre will not turn into calcite.

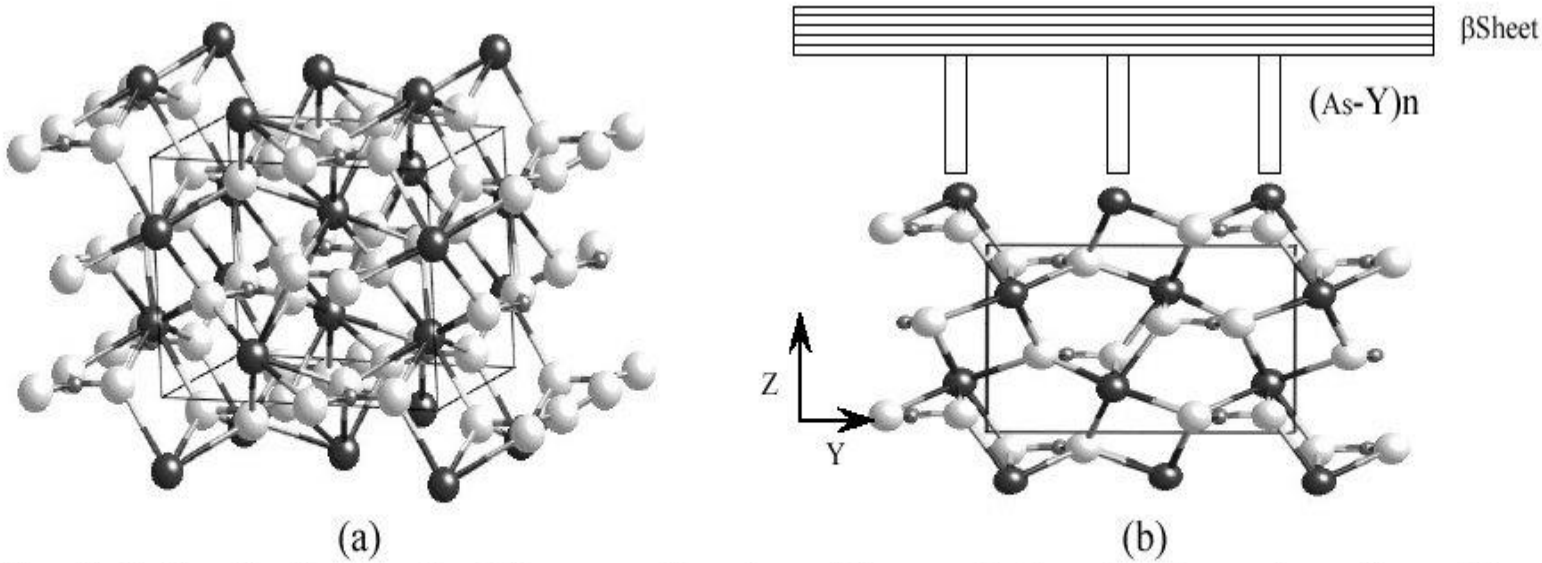
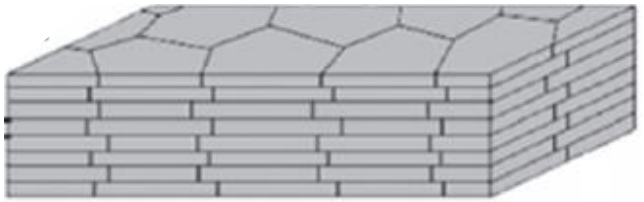


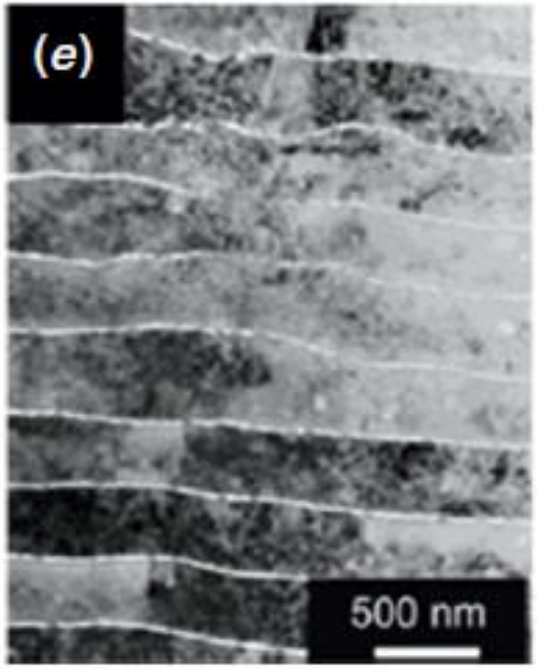
Fig. 5. Unit cell of aragonite; (a) perspective view; (b) normal view showing schematic position of $(Asp\text{-}Y)_n$ and β sheet. Notice protruding calcium ions on (001) face; black atoms: Ca; small black: carbon; gray atoms: oxygen. (courtesy of K. S. Vecchio, UCSD).

7. Bioceramics

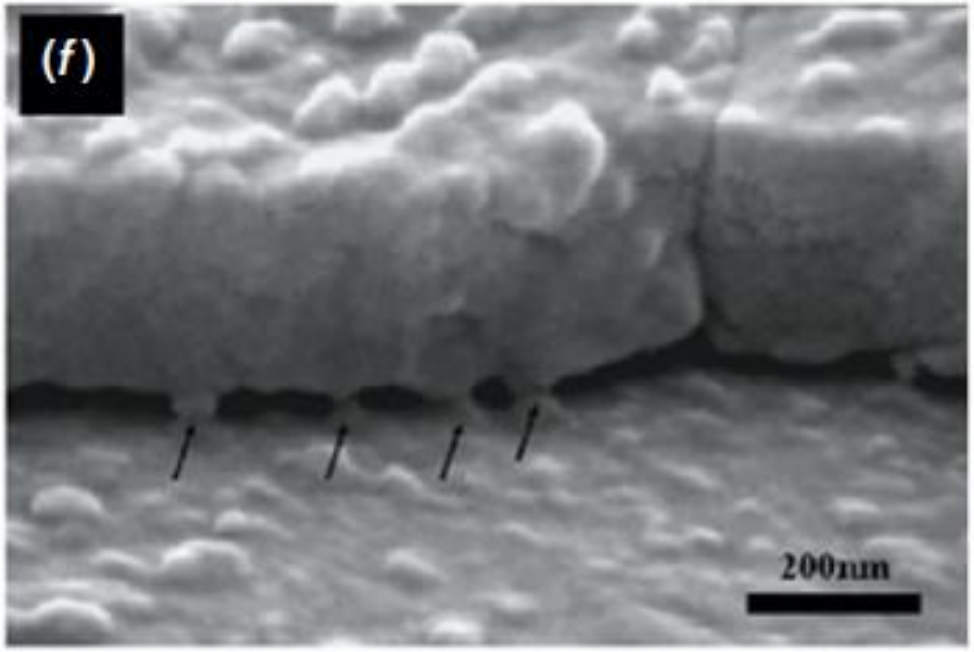
Mineral platelet surface in nacre

Smooth appearance at first sight, but…





Waviness on the micrometer scale

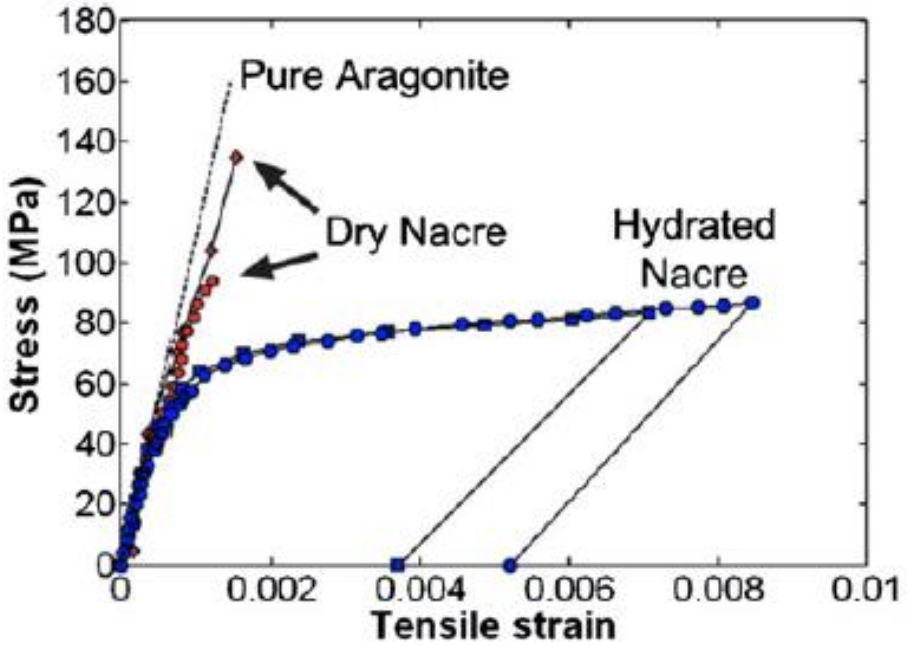


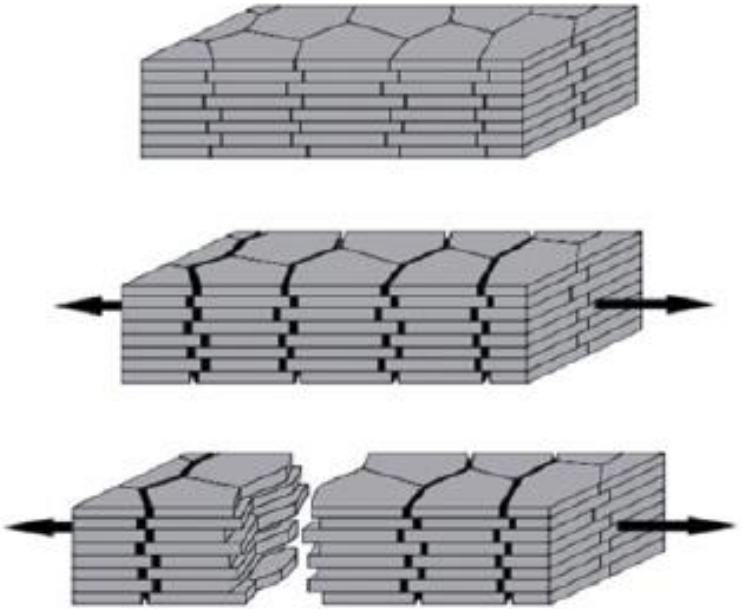
Asperities and mineral bridges on the nanometer scale

7. Bioceramics

Nacre in tension

- Dry nacre: similar to bulk aragonite, brittle failure
- Hydrated nacre: extensible to much larger strains (10 x strain of dry material), gliding of platelets





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7. Bioceramics

Mechanical performance of nacre

Only ca. 1% organic material yields increase of hardness by factor 3, increase of maximum strain by factor of 10, increase of toughness by factor 3000 as compared to pure aragonite!

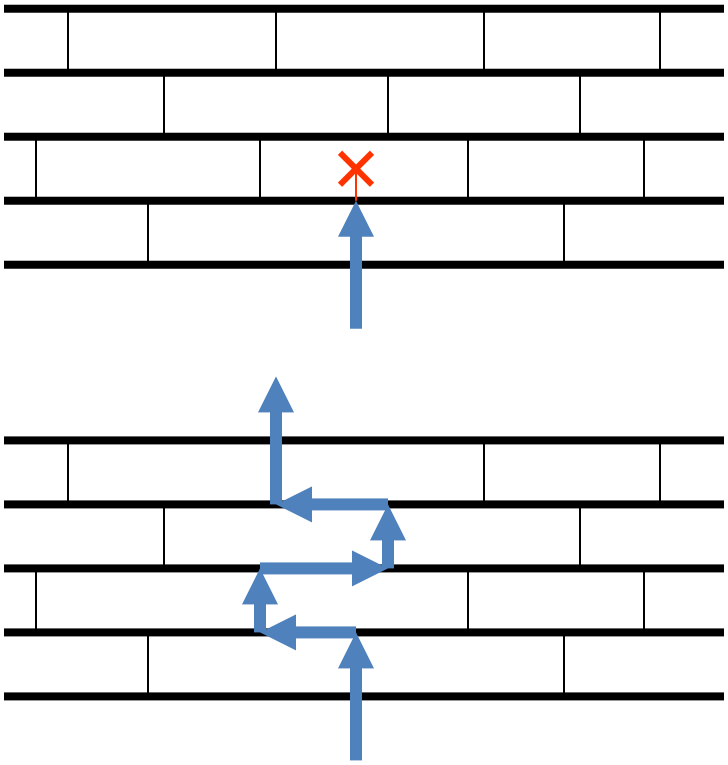
Mechanisms to increase toughness in nacre

- Deviation of crack path
- Deformation of organic phase
- Platelet pullout
- Platelet interlocking
- Microbuckling

7. Bioceramics

Deviation of crack path

Complicated fracture surface, platelet pull-out



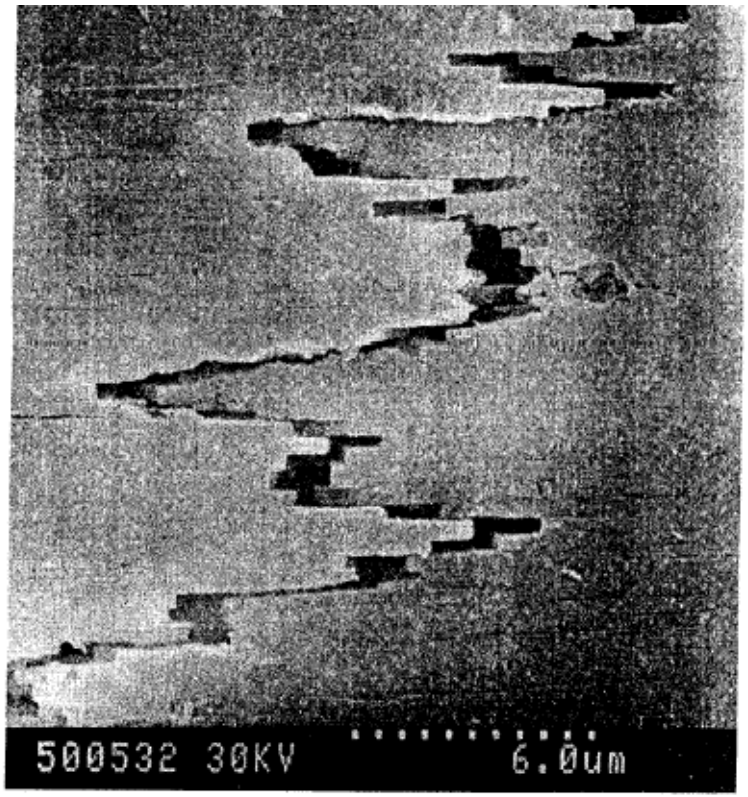
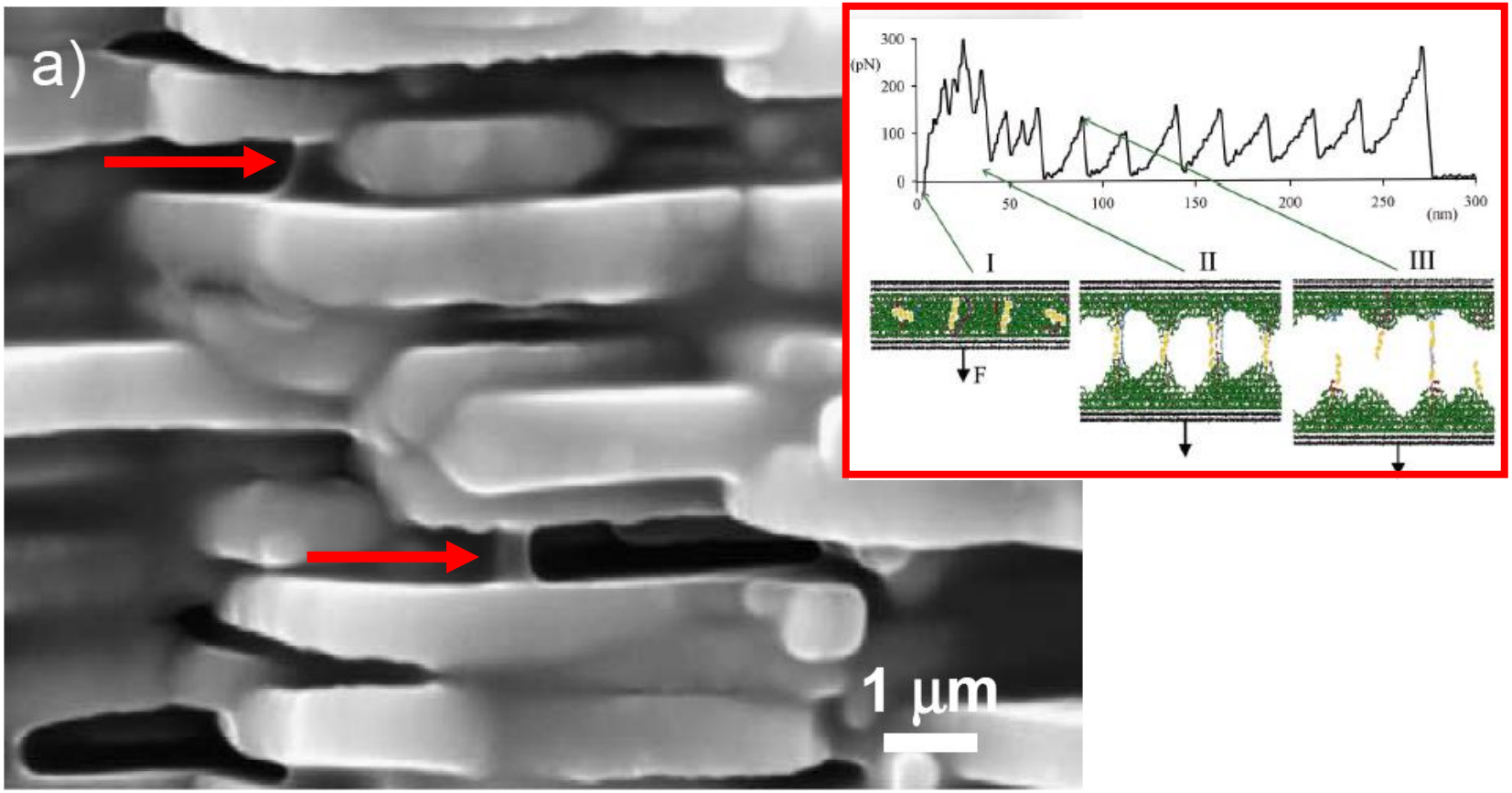


Figure 6.8 Fracture path through nacre viewed in orientation A (Fig. 6.3) (Jackson *et al.* 1988).

7. Bioceramics

Deformation of organic phase

Scanning electron microscope images of fracture surfaces of nacre:



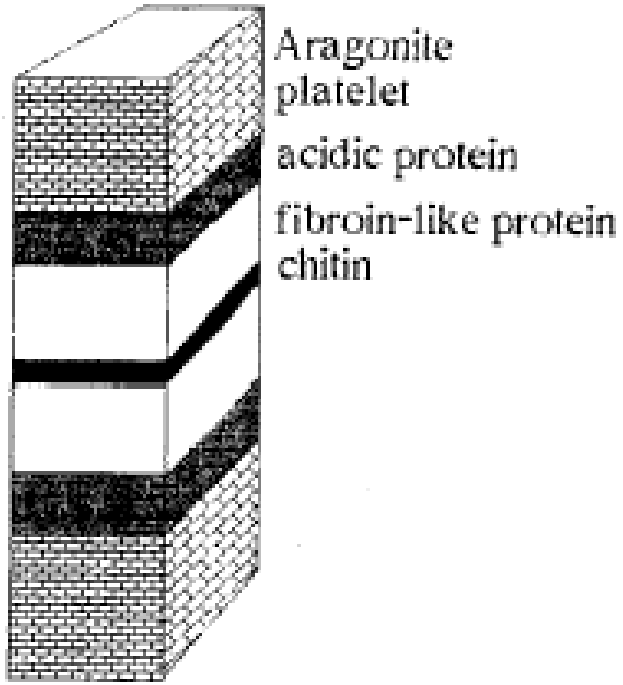
From: Katti&Katti, Mat Sci Eng C (2005)

7. Bioceramics

Organic phase in nacre

Layered structure:

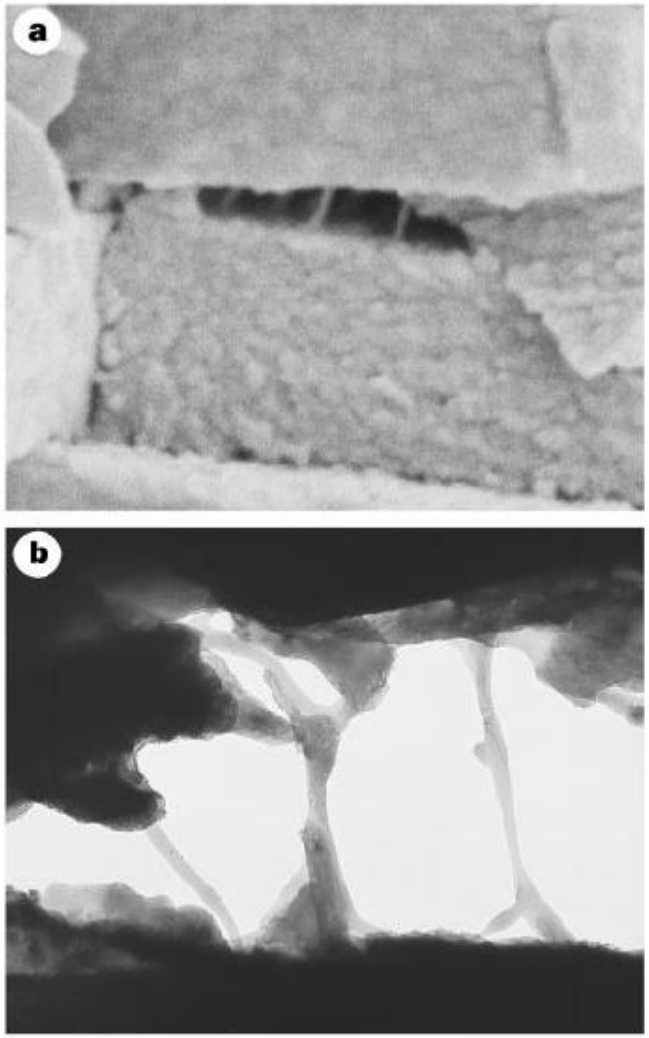
Model for the matrix material between two plates of nacre, showing acidic and fibroin-like proteins with chitin centrally (Weiner & Traub 1984).



7. Bioceramics

Deformation of organic phase in nacre

Crack bridging



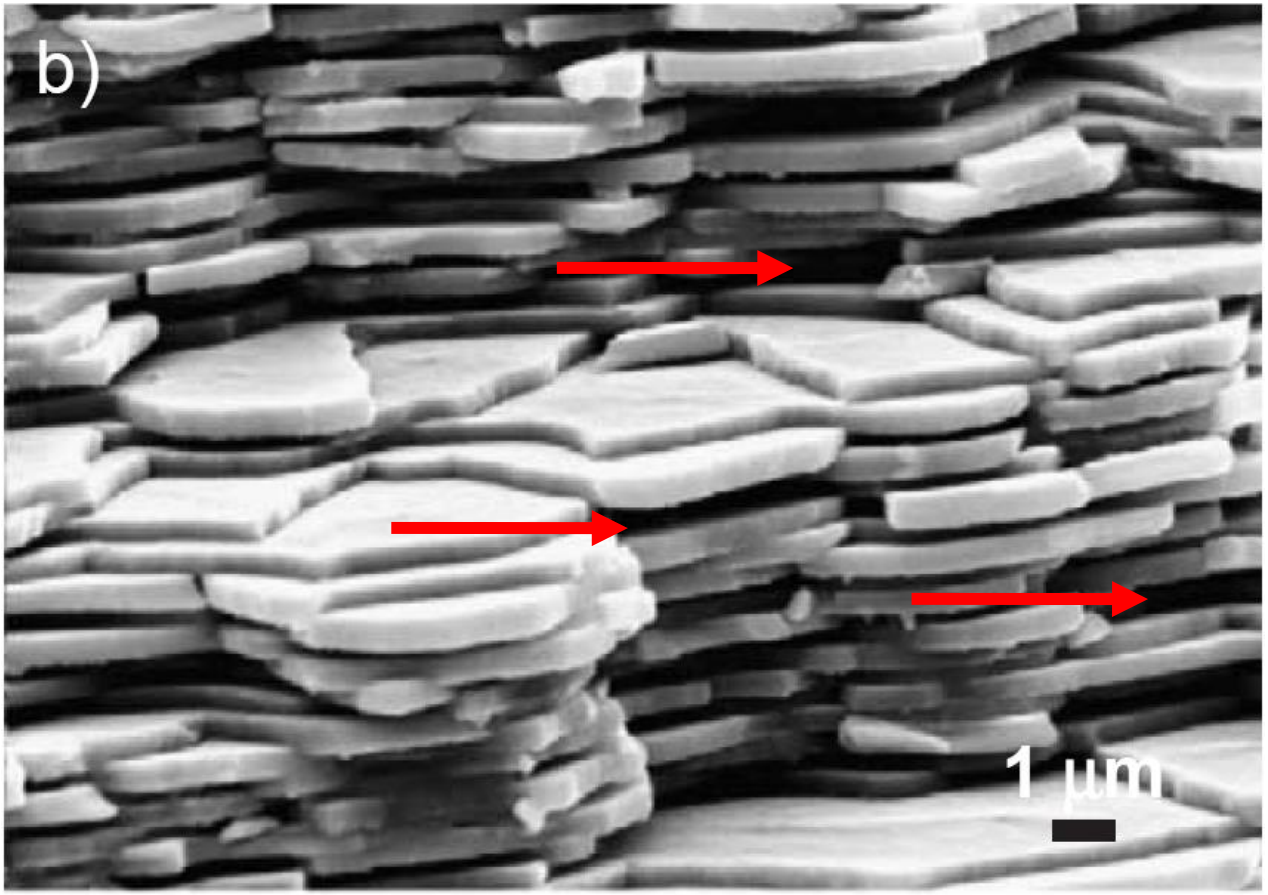
(a) SEM of freshly cleaved abalone shell showing adhesive ligaments formed between abalone nacre tablets

(b) TEM of cleaved abalone shell, showing the adhesive ligaments between nacre tablets. The space between the tablets is about 600 nm. Thus the ligaments can extend many times the original spacing between the tablets, which is of the order of 30 nm.

7. Bioceramics

Platelet pullout

SEM image of fracture surface

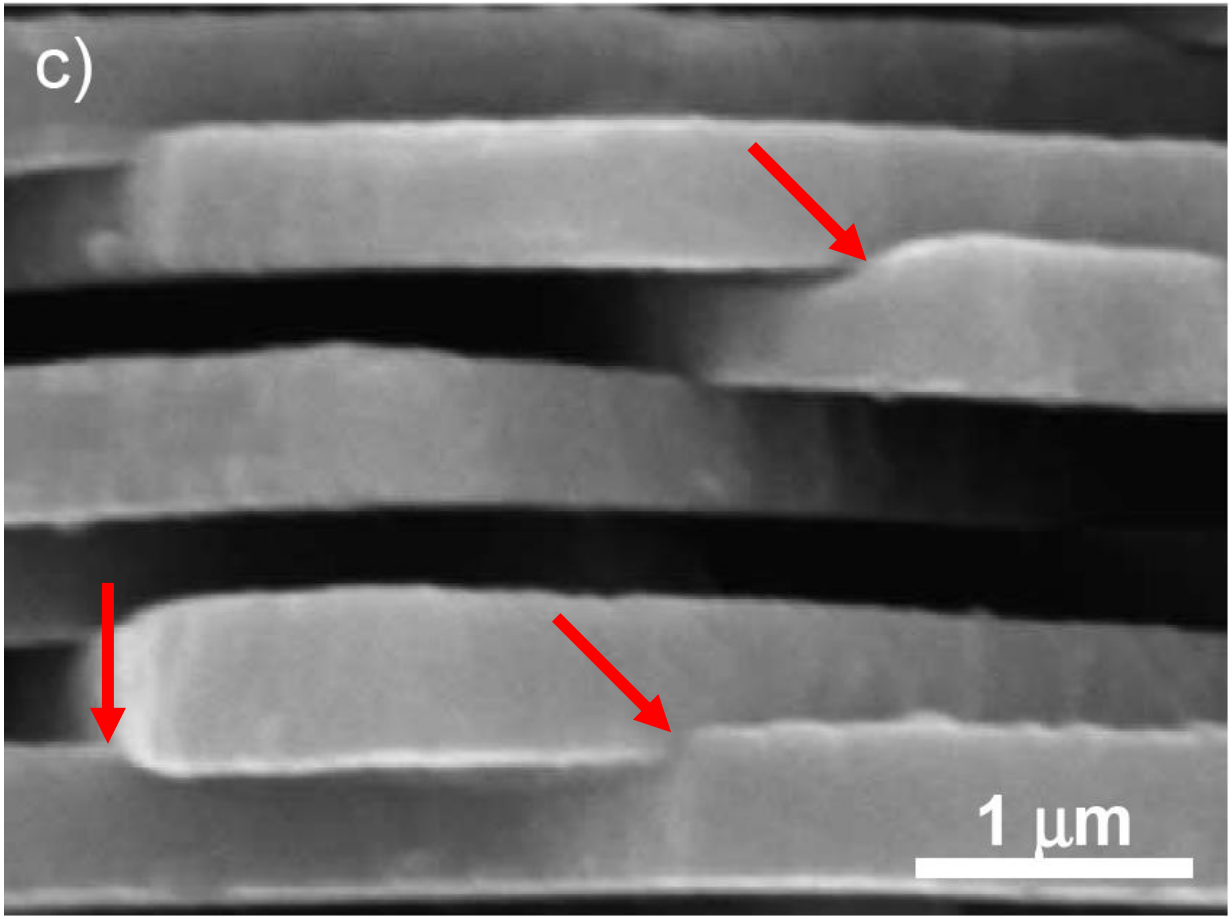


From: Katti&Katti, Mat Sci Eng C (2005)

7. Bioceramics

Platelet interlocking

SEM image of fracture surface: crack may be stopped by interlocking of platelets

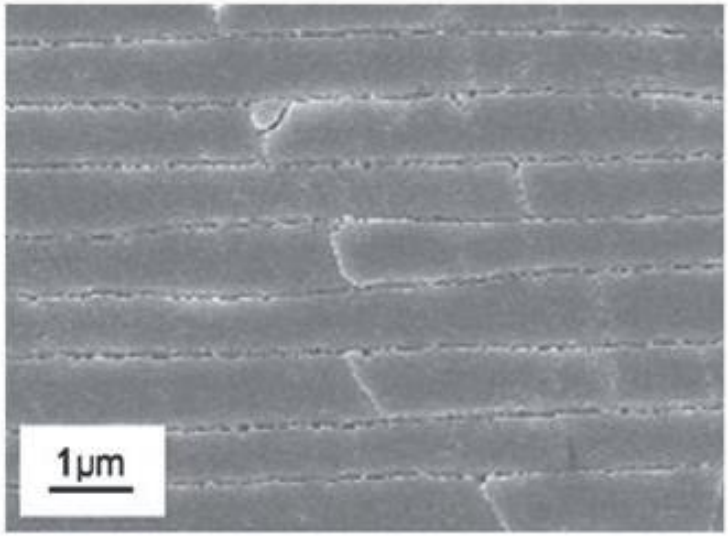


From: Katti&Katti, Mat Sci Eng C (2005)

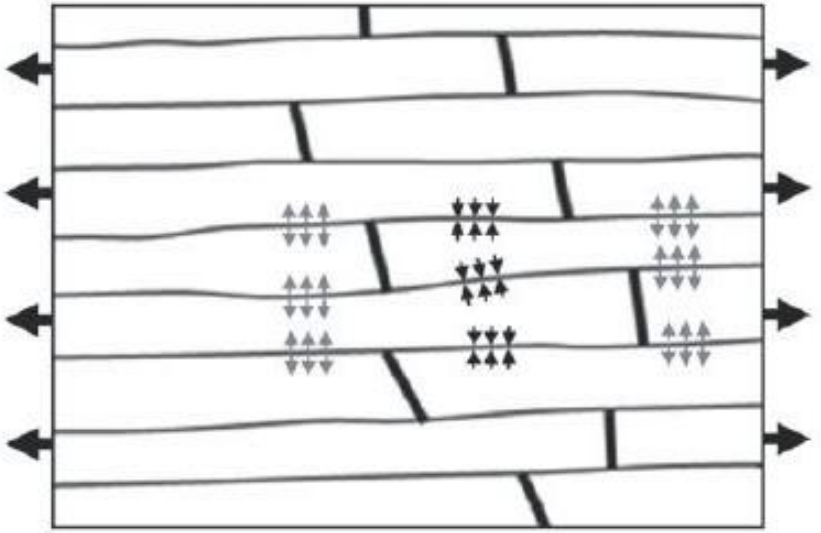
7. Bioceramics

Platelet interlocking

Leads to spreading of the gliding process throughout material. Hardening at higher strains through progressive tablet locking, also generatedby waviness of tablets.



(a)



(b)

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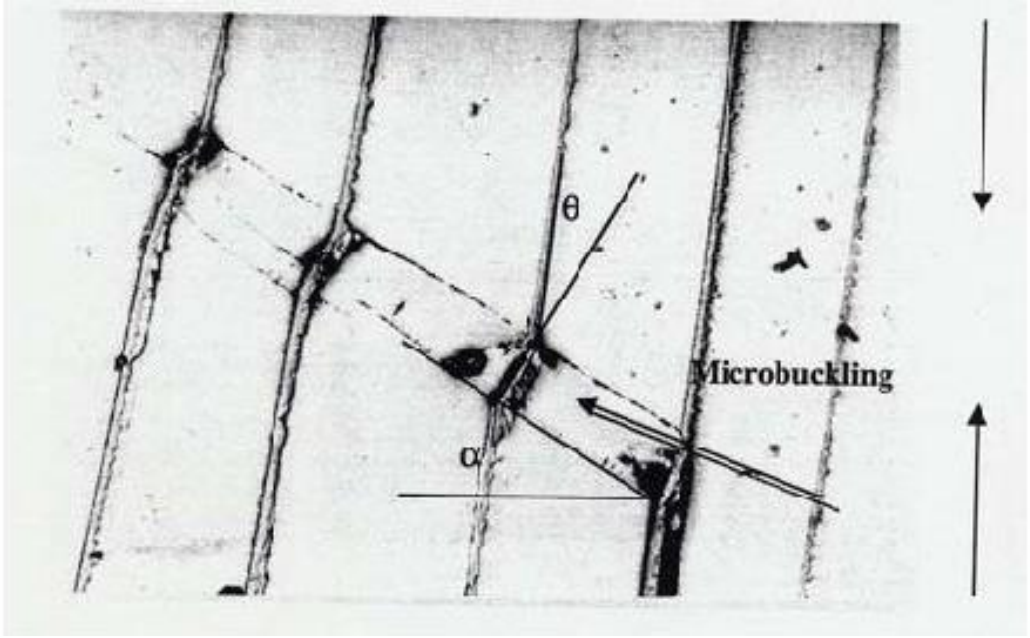
7. Bioceramics

Microbuckling in nacre

Failure remote from crack

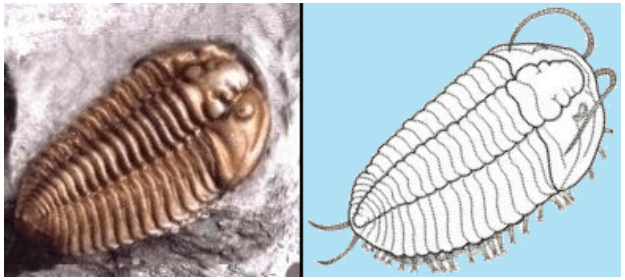


7. Bioceramics

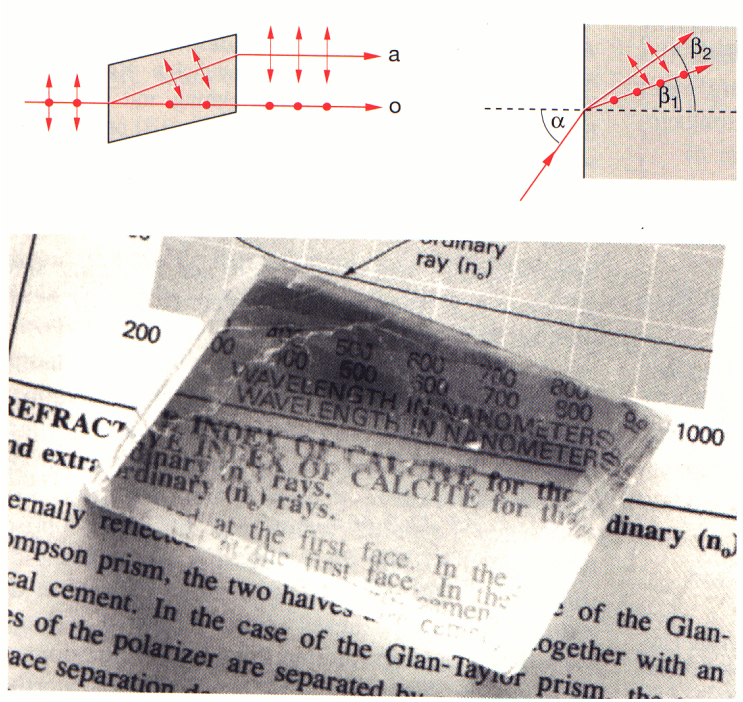
7.3.2 Mineral for optics, calcitic lenses

Trilobites: hard-shelled, segmented organisms that existed over 300 million years ago in the Earth's ancient seas - key signature creatures of the Paleozoic Era.

Calcitic lenses: trilobites had eyes equipped with mineralized (calcite) lenses



Optical properties of calcite: birefringent!



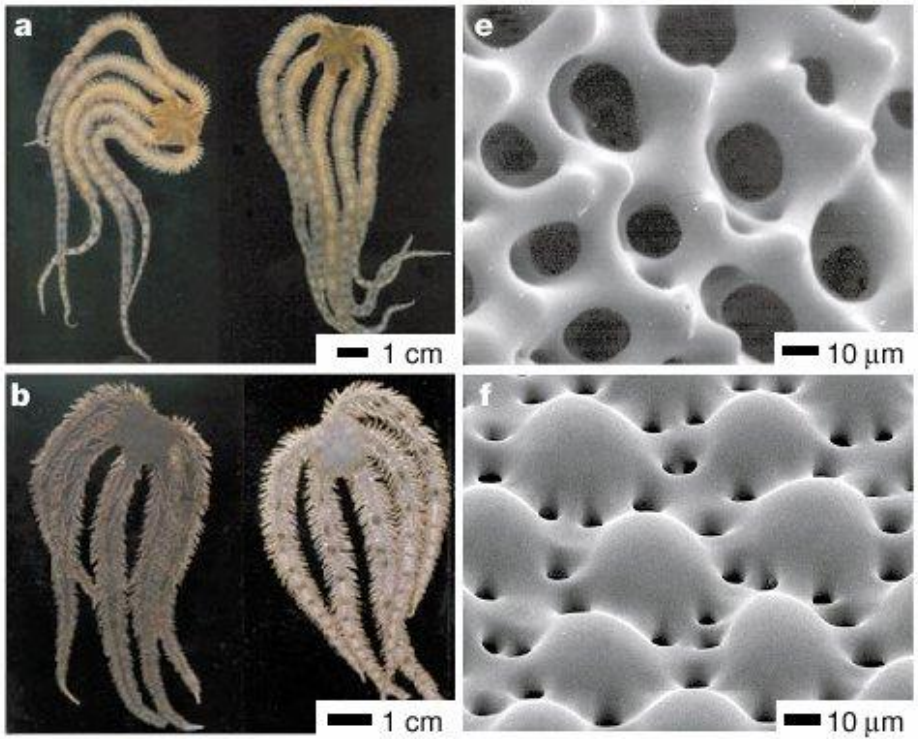
Orientation of calcite lenses such that light entered parallel to main optical axis (no birefringence)

7. Bioceramics

Calcitic microlenses in brittlestar

Exterior skeleton made from lenses. These structures represent an example of a multi-functional biomaterial that fulfills both mechanical and optical functions.

a), e): light-indifferent species (*Ophiocoma pumilla*)



b), f): light sensitive species (*Ophiocoma wendtii*): changes color upon irradiation with light

7. Bioceramics

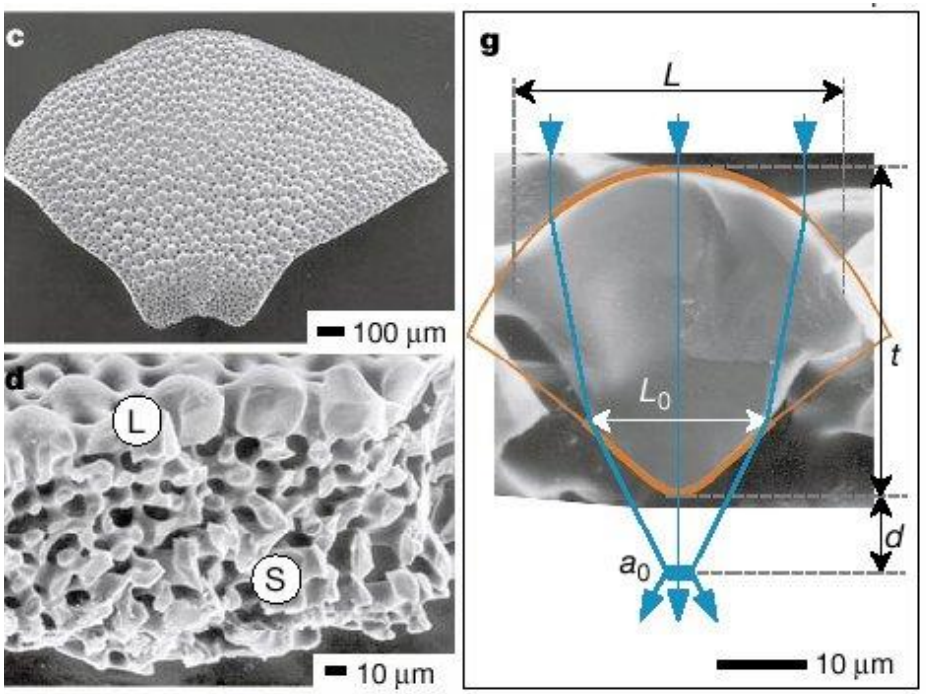
Calcitic microlenses in brittlestar

Calcite crystal oriented with main axis in direction of incoming light. Lenses formed such that they focus light on fluorescent dye containing layer.

(c) SEM of a dorsal arm plate (DAP) of O. wendtii cleansed of organic tissue.

(d) SEM of the cross section of a fractured DAP from O. wendtii showing the typical calcitic stereom (S) and the enlarged lens structures (L).

(g) High-magnification SEM of the cross-section of an individual lens in O. wendtii. Red lines represent the calculated profile of a lens compensated for spherical aberation. The operational part of the calcitic lens (L0) closely matches the profile of the compensated lens (bold red lines).



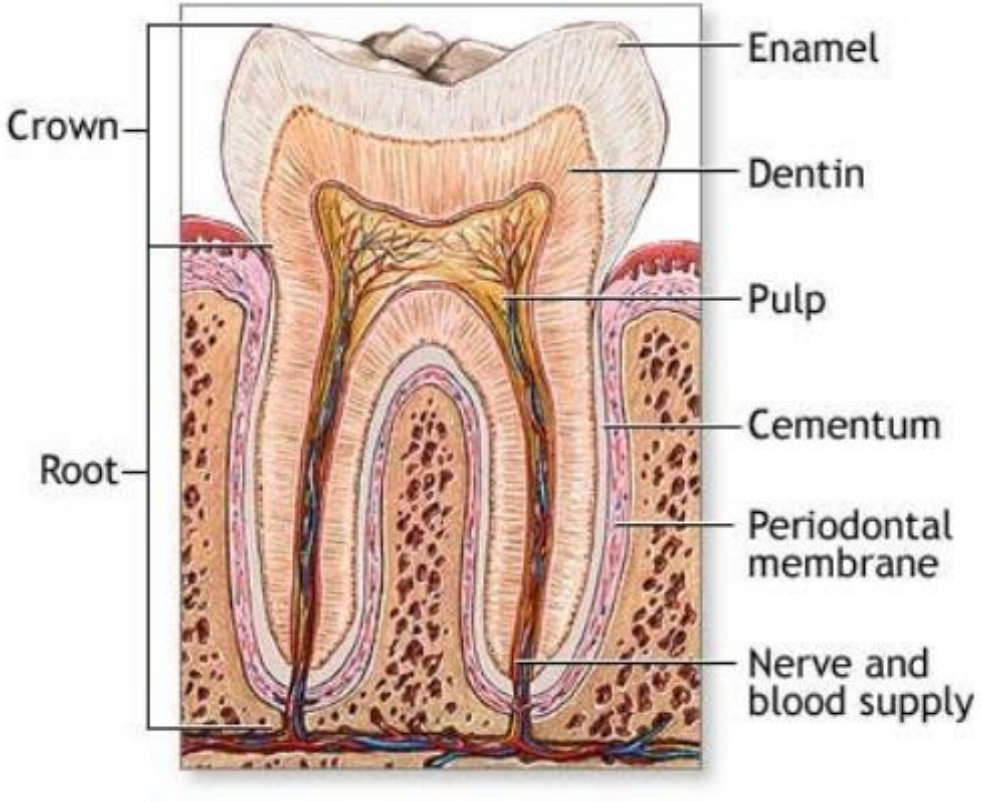
7. Bioceramics

7.3.3 Vertebrate teeth

Vertebrate teeth consist of two types of hard material:

Enamel: top coat, white appearance, hard and highly mineralized

Dentin: mineral underneath, softer, bone-like



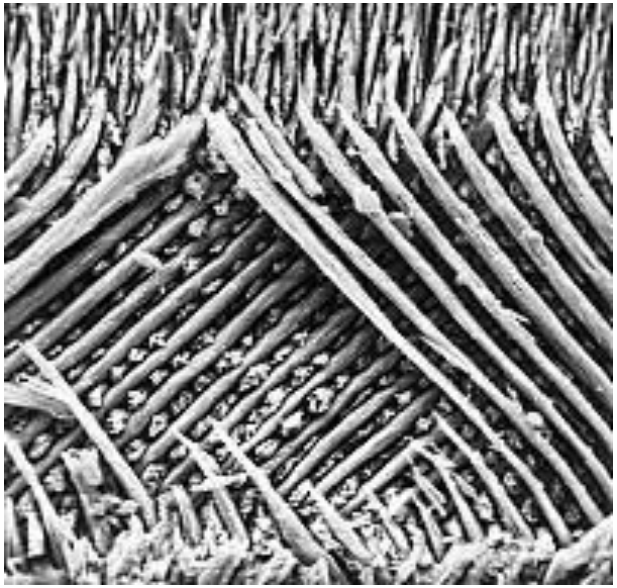
7. Bioceramics

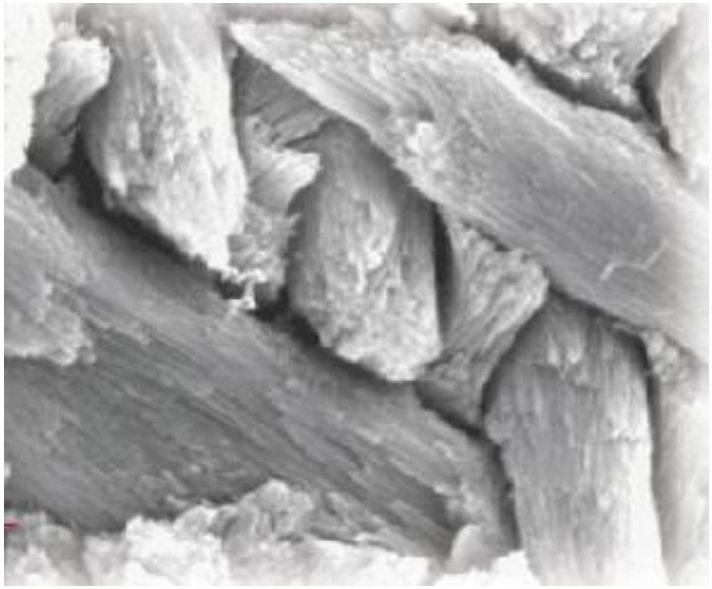
Tooth enamel

Consists of relatively large crystals of hydroxyapatite (same mineral as in bone), but in much higher quantity.

Enamel contains only about 2% vol of protein and very little water.

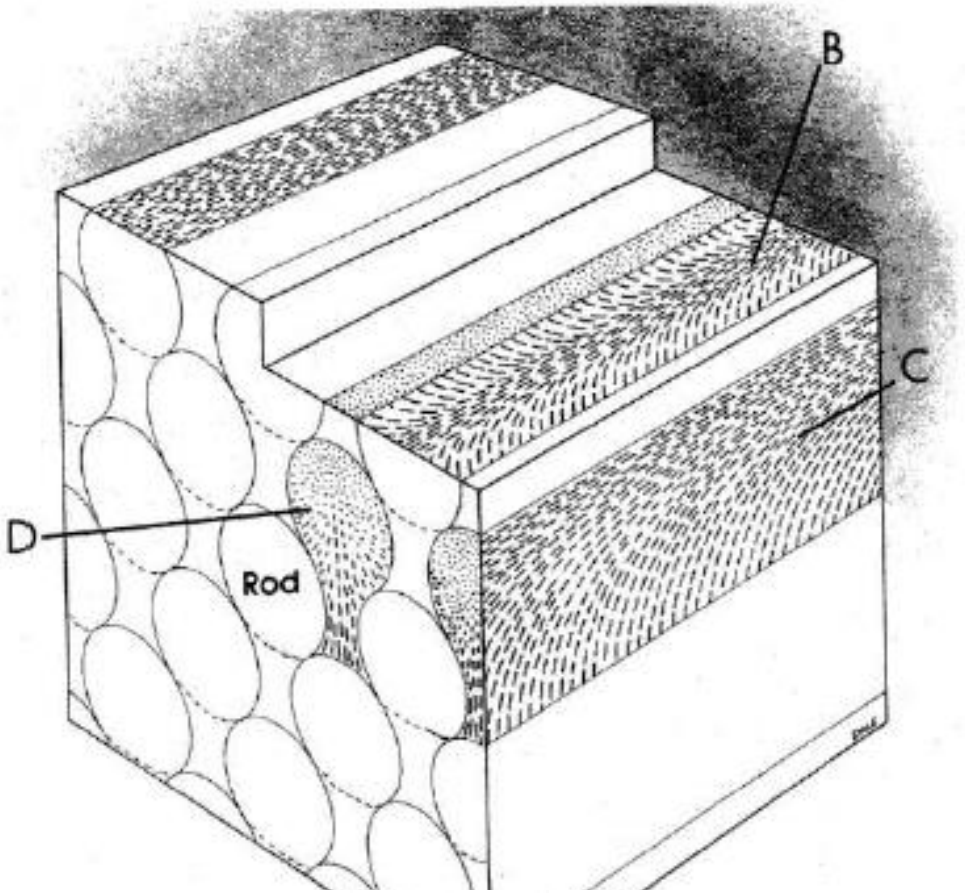
Structure: plywood arrangement of micrometer sized mineral rods (enamel rods)

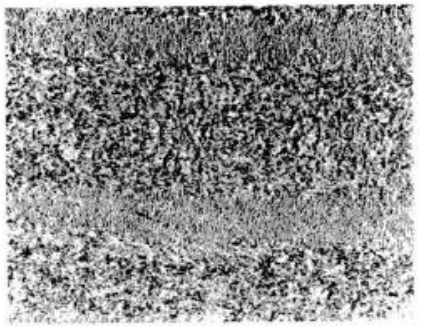


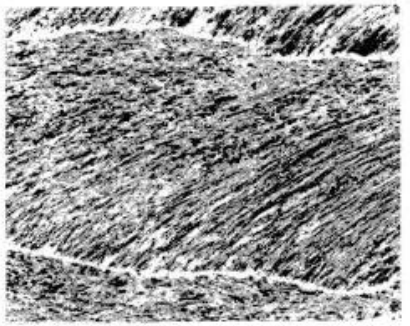


7. Bioceramics

Fine structure of enamel rods







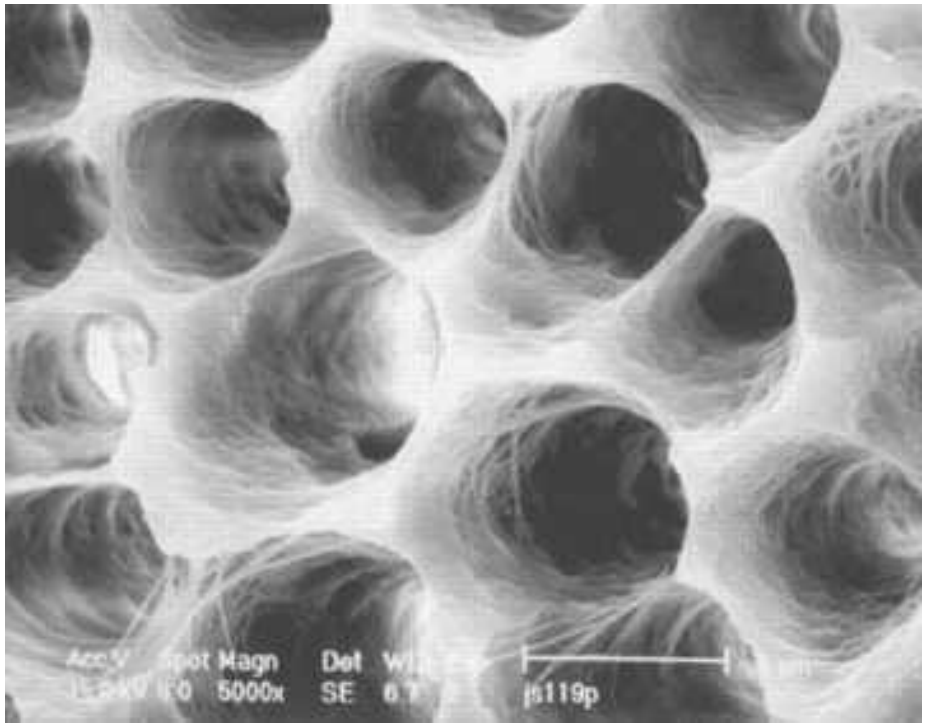
A

Figure 11-6 Fine structure of enamel. **A**, Crystal orientation of three faces of a block of enamel, showing the rod structure. **B** to **D**, Electron micrographs of three faces. (Courtesy Dr. AH Meckel.)

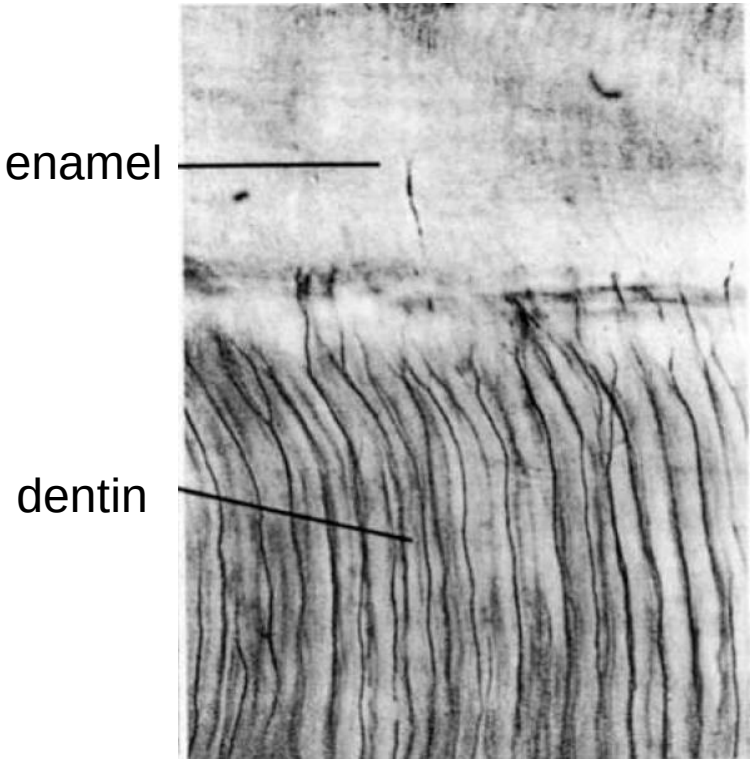
7. Bioceramics

Dentin

Bone like material with tubular microstructure. Growth: from outside to inside.



Tubular structure of dentin in cross section



Dentin enamel junction in longitudinal section

7. Bioceramics

Comparison bone – dentin - enamel

Composition and mechanical properties

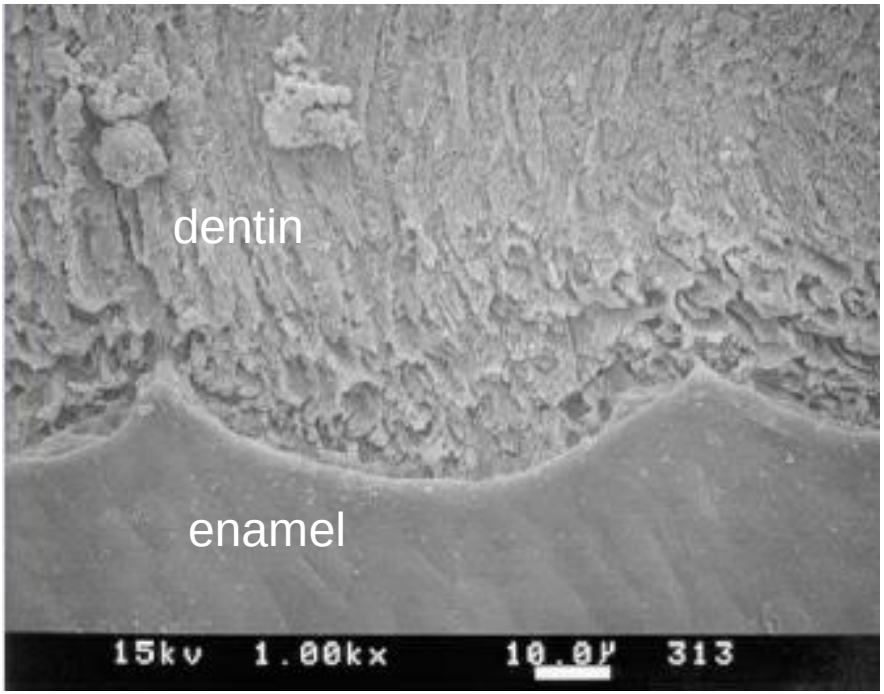
	bone	dentin	enamel
HAP vol% (wt%)	41 (64)	48 (69)	92 (97)
Organic vol% (wt%)	48 (31)	29 (20)	2 (1)
Water vol% (wt%)	11 (5)	23 (11)	6 (2)
Youngs modulus GPa	17-20	10-20	75-90
Tensile strength MPa	150	30-100	8-35
Compressive strength MPa	220	250-350	200-400

7. Bioceramics

Dentin – enamel junction (DEJ)

Problem: modulus mismatch, high stress concentration → may lead to delamination of enamel layer from dentin

Solution: mechanical gradient (also gradient in mineralization), toothed structure (approx. 40 μm) on micrometer scale, roughness on nanometer scale

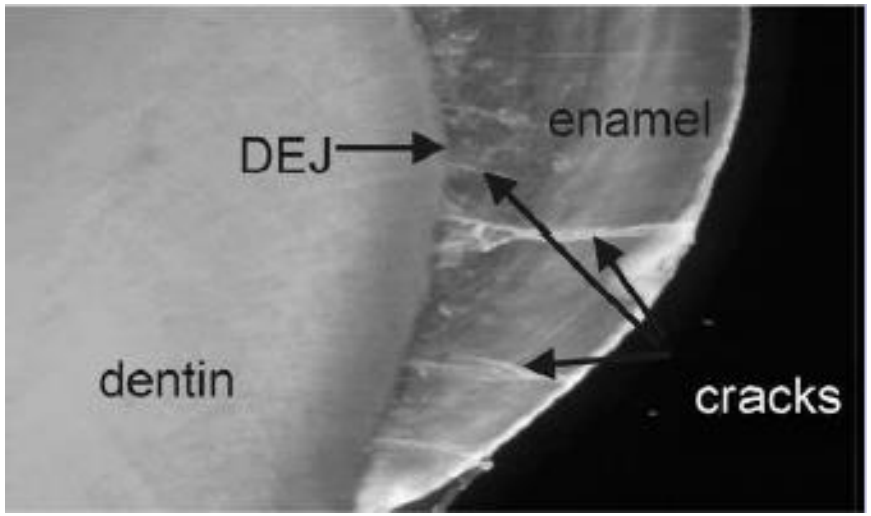


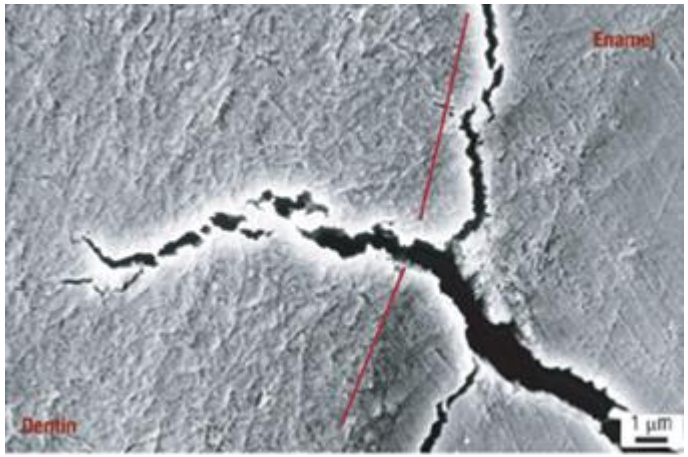
Courtesy Martin Bäker, TU-Braunschweig

7. Bioceramics

Dentin – enamel junction (DEJ)

Because of gradient material and roughess cracks get arrested at DEJ





V. Imbeni et al. (2005) The dentin−enamel junction and the fracture of human teeth. Nature Materials 4, 229–232.

7. Bioceramics

Formation of tooth enamel

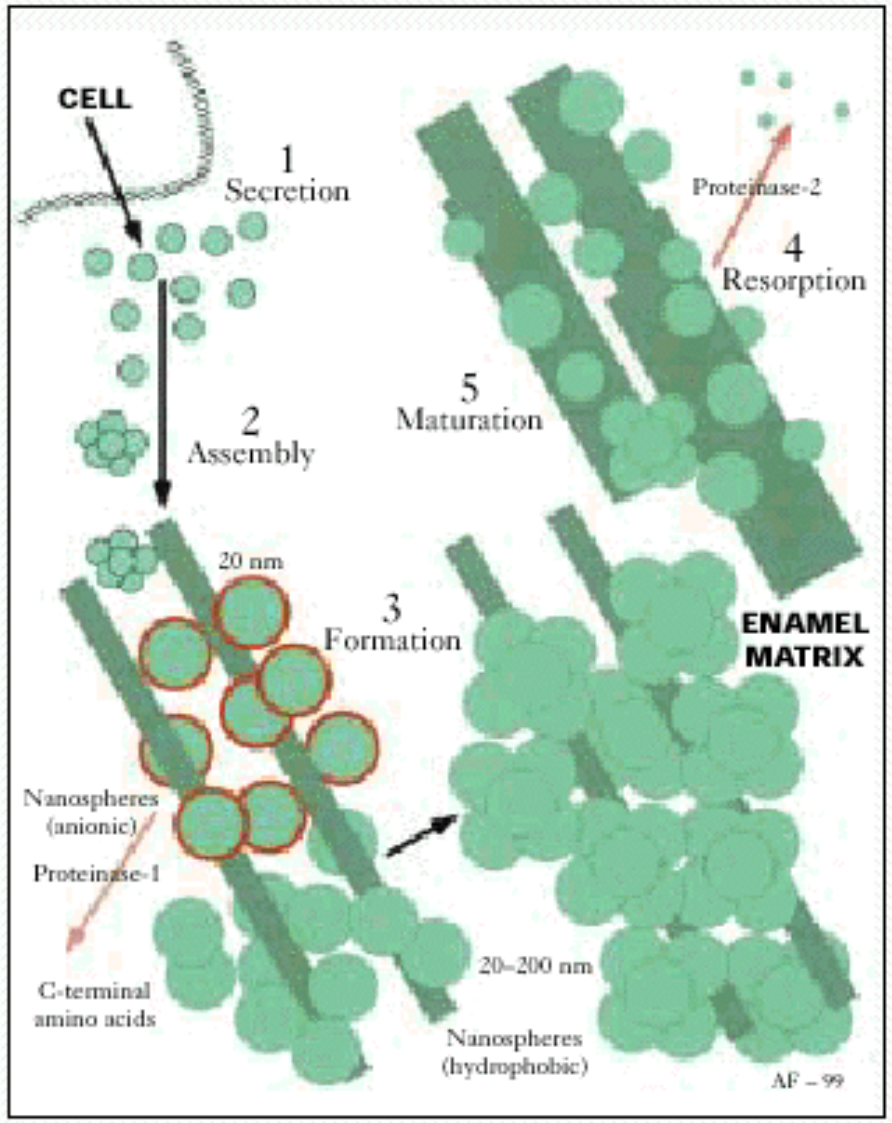
1. Amelogenins synthesized and secreted by ameloblast cells.

2. Amelogenin molecules assemble into nano-sphere structures approx. 20 nm in diameter with anionic surface.

3. Nanospheres interact electrostatically with elongating enamel crystallites, acting as 20 nm spacers preventing crystal-crystal fusions. Enzymes digest away charged surface of the nanospheres, producing hydrophobic nanospheres that further assemble and stabilize the growing crystallites.

4. Other enzymes (Proteinase-2) degrade hydrophobic nanospheres, generating amelogenin fragments and other products, which are resorbed by the ameloblasts.

5. As the amelogenin nanosphere protection is removed, crystallites thicken and eventually may fuse into mature enamel.



7. Bioceramics

Composition of enamel during formation

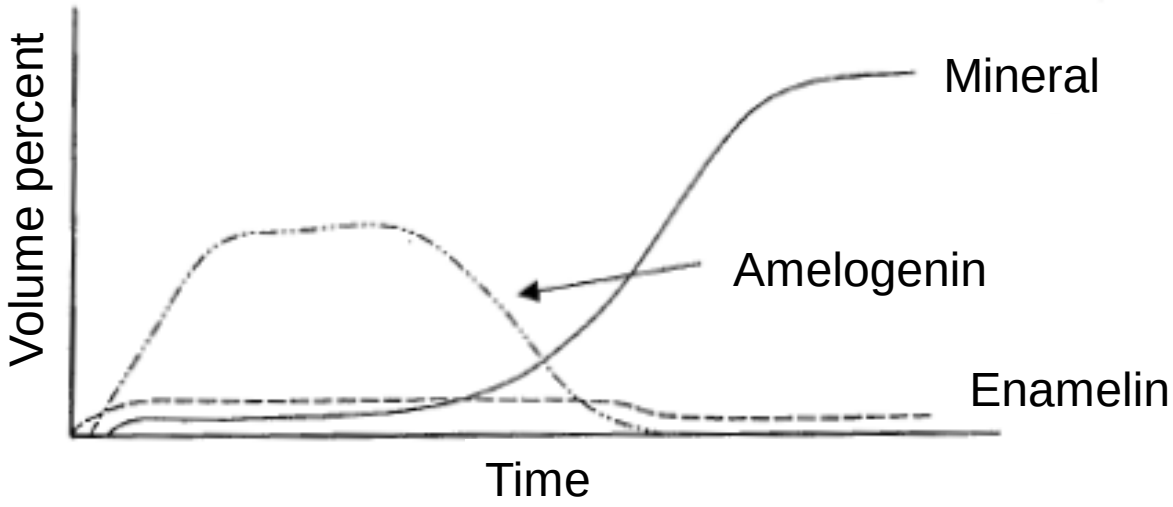


Fig. 2.13 Loss of proteins and increase in mineral content with time during enamel formation.

7. Bioceramics

Composition of different vertebrate enamels

Compare human teeth to shark teeth:

Fish teeth are very similar to enamel (enameloid), but contain much more fluoride, eg. shark: fluoride concentration is over one 1000 times that in human enamel

Table 2.3 Chemical composition of calcium phosphate (hydroxyapatite) in human and shark enamel

Composition (wt%)	Human enamel	Shark enamel
Ca^{2+}	37.55	37.26
Na^{+}	0.75	0.76
Mg^{2+}	0.27	0.32
PO_4^{3-}	17.68	17.91
CO_3^{2-}	3.6	1.1
F^{-}	0.02	3.65

Shark: No fluoride treatment necessary

7. Bioceramics

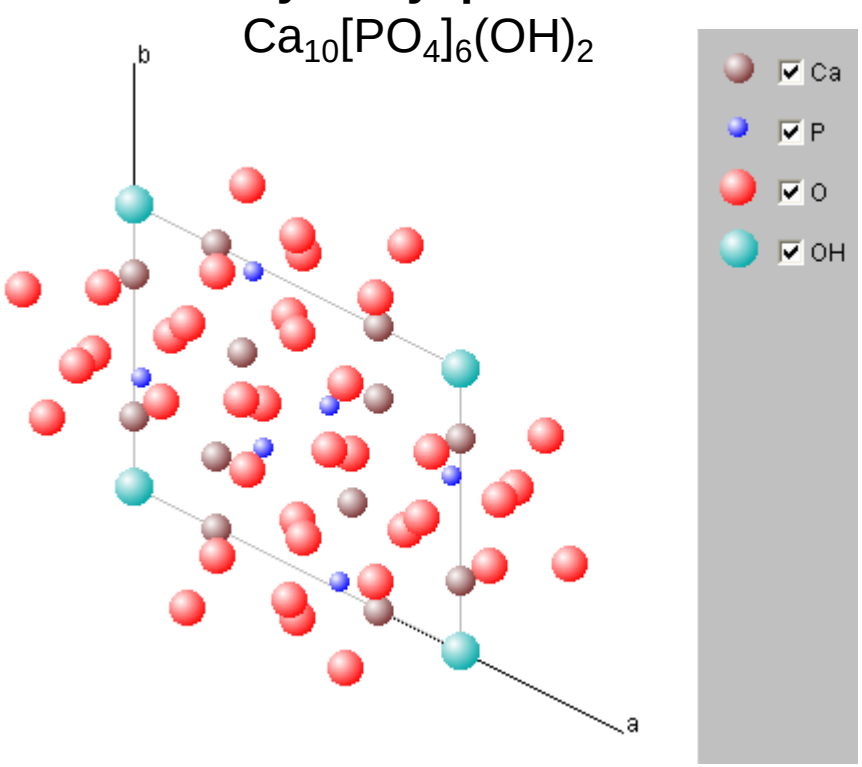
Why do human teeth need fuoride treatment?

Hydroxyapatite (HAP) affected by acids (solubility is pH dependent).

Much less so for Fluorapatite (OH group in HAP replaced by fluoride)

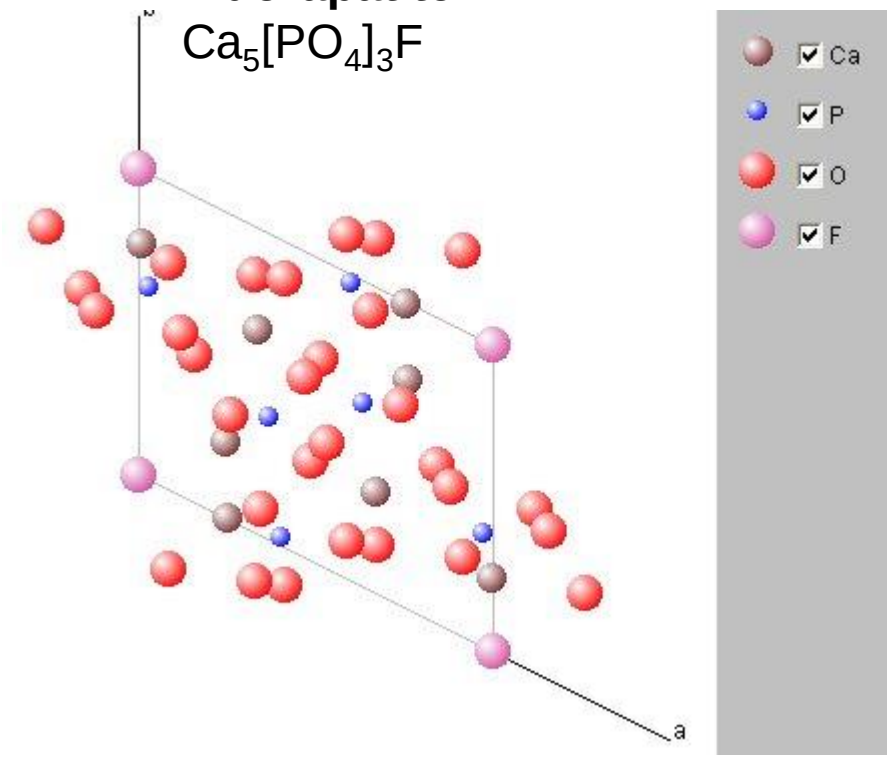
Hydroxyapatite

$Ca_{10}[PO_4]_6(OH)_2$



Fluorapatite

$Ca_5[PO_4]_3F$



7. Bioceramics

7.3.4 Metal based teeth

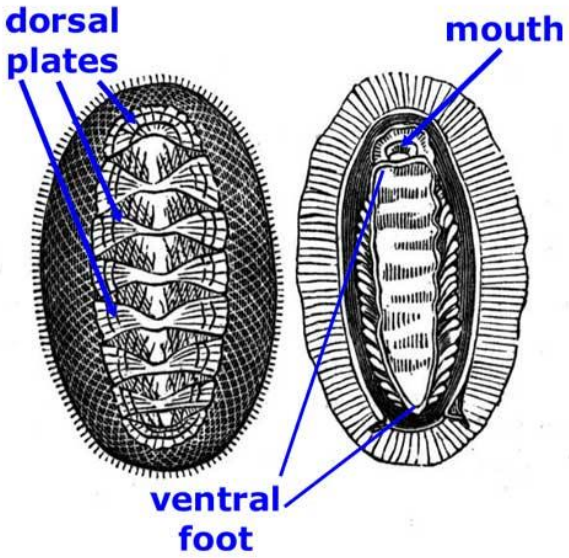
… actually metal oxide based teeth…

7. Bioceramics

Iron oxides in radula of chitons

Iron oxide minerals are found as outermost coating of chitons (marine molluscs) that live from scraping algae from rocks.

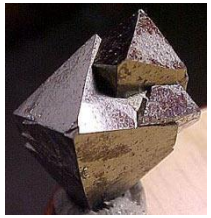
chiton



Radula: tongue like organ equipped with teeth

Iron minerals:

magnetite Fe_3O_4



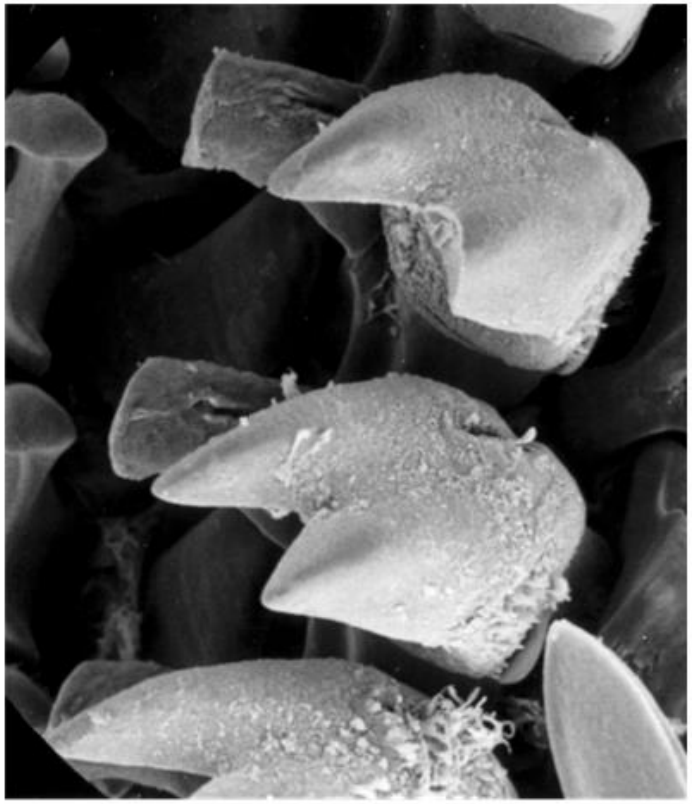
Lepidocrocite
β-FeOOH

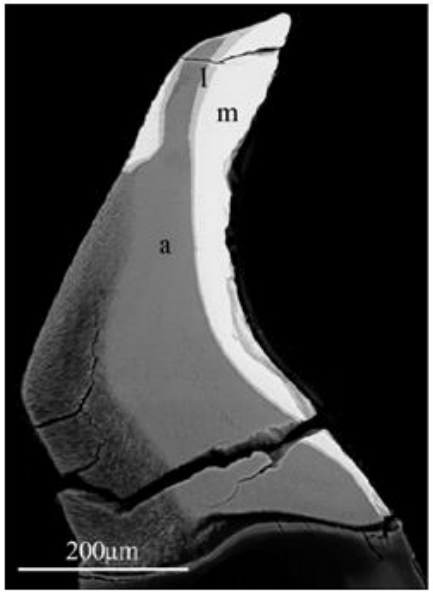
Resulting magnetic moment: radula can be picked up with a magnet! – without the attached organism....

7. Bioceramics

Structure and compositon of chiton tooth

Teeth contain various biominerals: iron oxides at the cutting edge, deposits of hydroxyapatite in the back





m: magnetite
l: lepidocrocite
a: apatite

image courtesy of Tom Ford, University of Dundee, U.K.

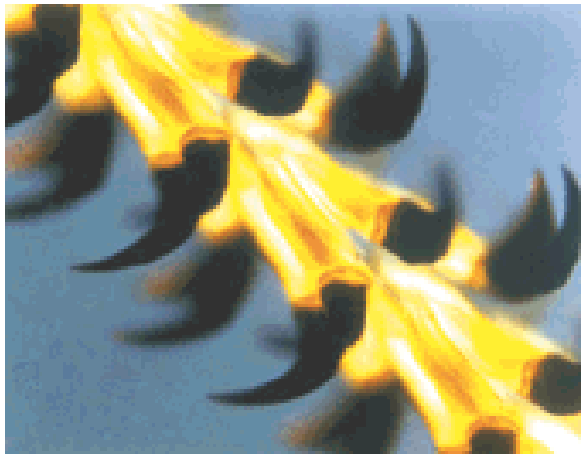
R.J. Wealthall, L.R. Brooker, D.J. Macey, and B.J. Griffin (2005). Fine structure of the mineralized teeth of the chiton Acanthopleura echinata (Mollusca : Polyplacophora). Journal of Morphology 265 (2), 165-175.

7. Bioceramics

Radula of limpets

Limpets: radula 7 cm long, contains hundreds of teeth, feed from algae growing on rocks, uses teeth to scrape the algae from substrate

limpet



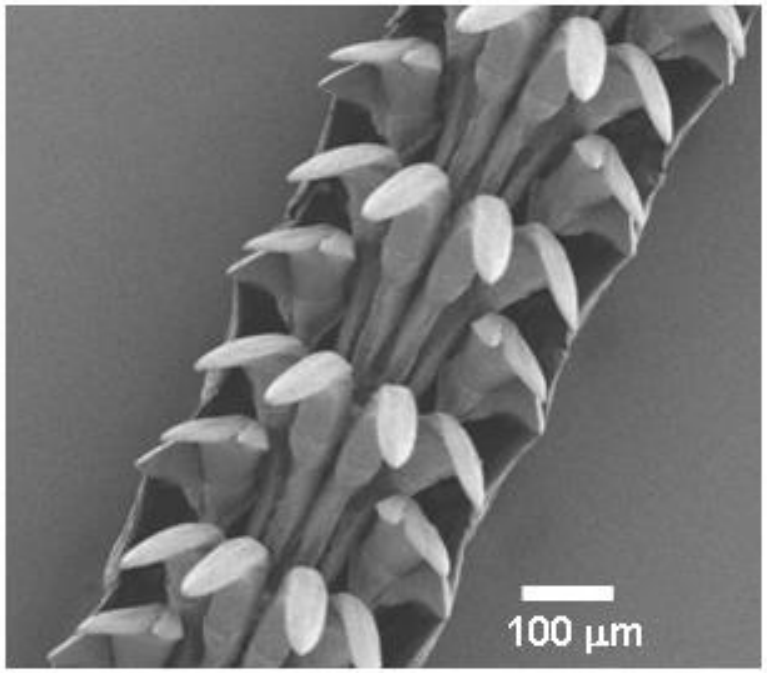
radula

goethite
α-FeOOH

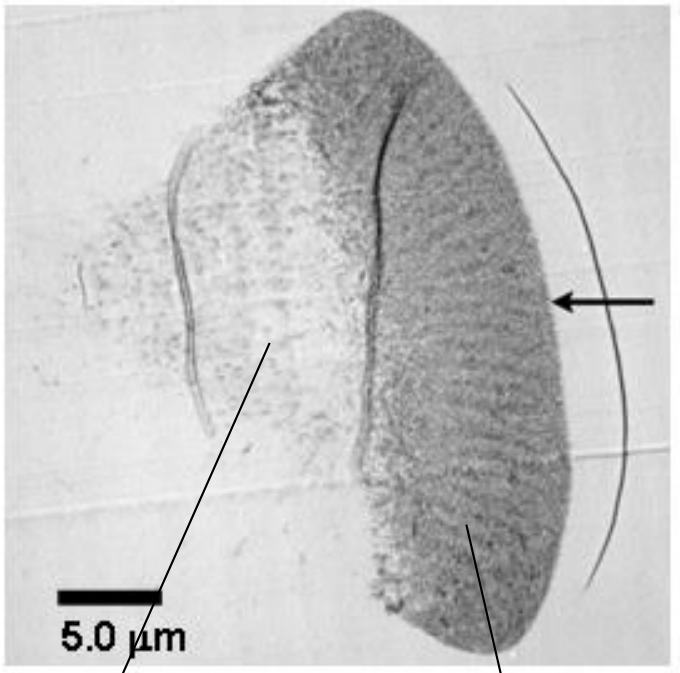
7. Bioceramics

Structure and compositon of limpet tooth

Teeth contain iron oxide goethite at the cutting edge, silica in the back



Limpet radula



silica (SiO_2)

goethite

E.D. Sone, S. Weiner, and L. Addadi (2005). Morphology of goethite crystals in developing limpet teeth: Assessing biological control over mineral formation. Crystal Growth & Design 5 (6), 2131-2138.

7. Bioceramics

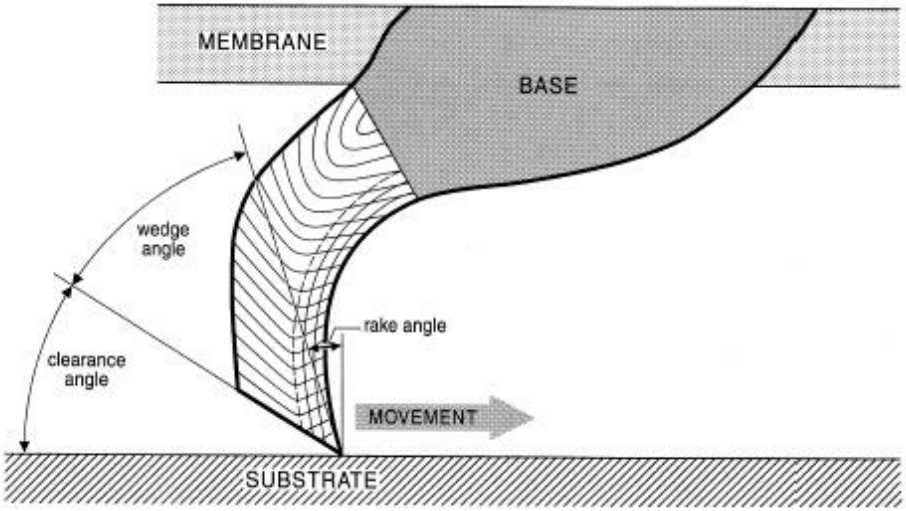
Why use iron minerals?

Compare hardness of different minerals:

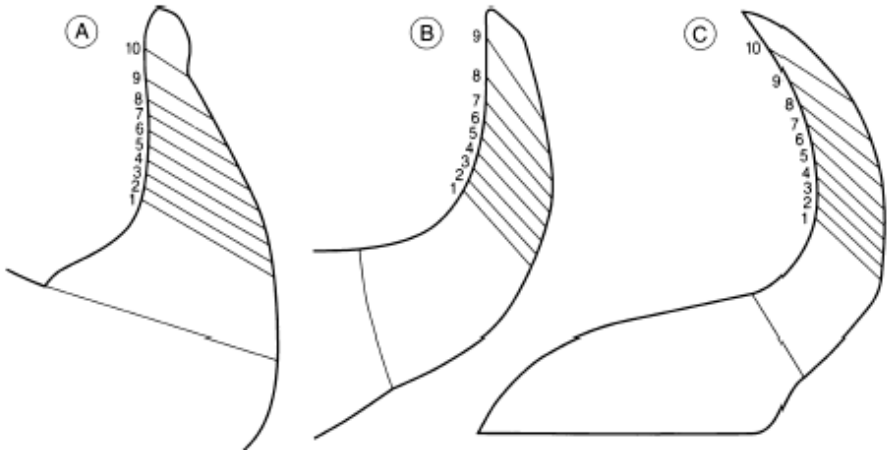
Mineral	Mohs Hardness
Calcite ($CaCO_3$)	3
Apatite, hydroxy-apatite	5
Lepidocrocite (g-FeOOH)	5
Goethite (a-FeOOH)	5 – 5.5
Magnetite (Fe_3O_4)	5.5 - 6

7. Bioceramics

Continuously sharp cutting edges



Schematic drawing of limpet mineralized tooth in grazing position. In this sagittal section of the cusp the orientations of the constructive elements are shown. Also shown are clearance, wedge and rake angels.

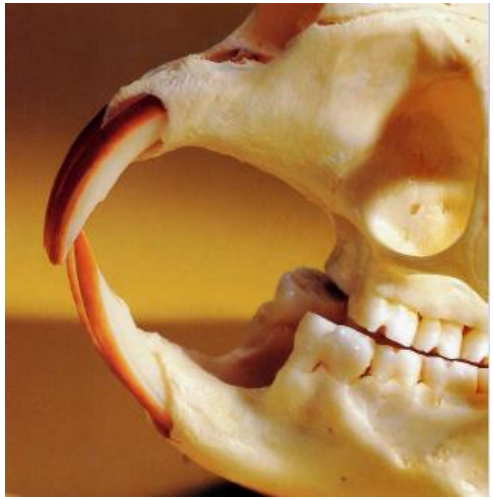


Schematic drawing of the orientations of the surface wear during the working life of a mineralized tooth of (A) *Chiton olivaceus*, (B) *Chiton tuberculatus* and (C) *Patella vulgata* (common limpet). The consecutive stages are numbered from high to low.

P. van der Wal, H.J. Giesen, and J.J. Videler (2000). Materials Science & Engineering C-Biomimetic and Supramolecular Systems 7 (2), 129-142.

7. Bioceramics

Sharp teeth in rodents



courtesy of Martin Bäker, TU Braunschweig

Example: American hedgehog

Alignment of structural elements ensures sharp edges

⇨ **Model for fabriction of industrial cutting devices?**

Did you know that...

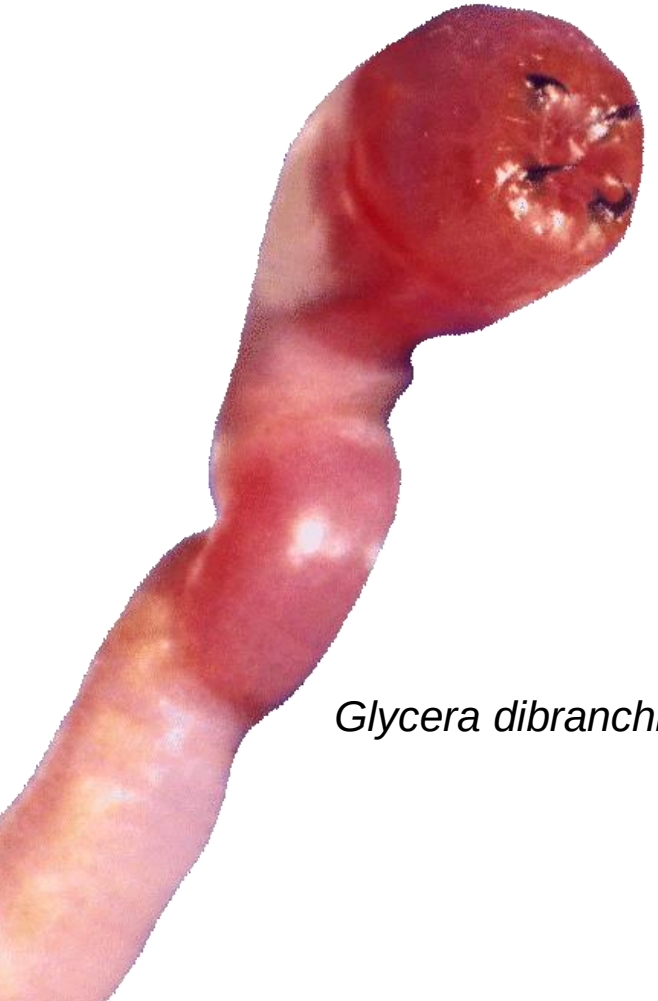
...some rodents (e.g. rats) also have iron compounds (ferrihydrite) in their teeth.
-> analogy to chitons and limpets ??

e.g. P.F. Heap, B.K.B. Berkovitz, M.S. Gillett, and D.W. Thompson (1983). Archives of Oral Biology 28 (3), 195-200.

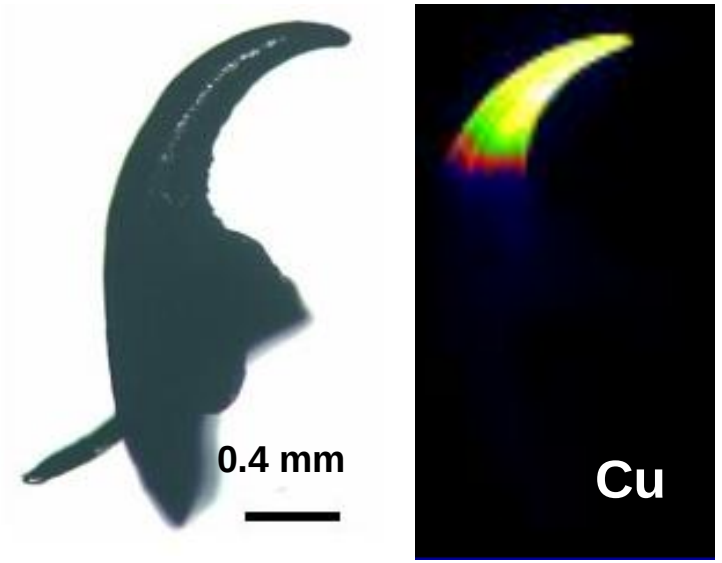
7. Bioceramics

Other metal containing teeth

Copper containing teeth of the marine worm Glycera:



Glycera dibranchiata



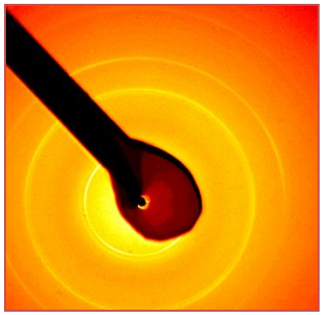
Up to 30% Cu w/w

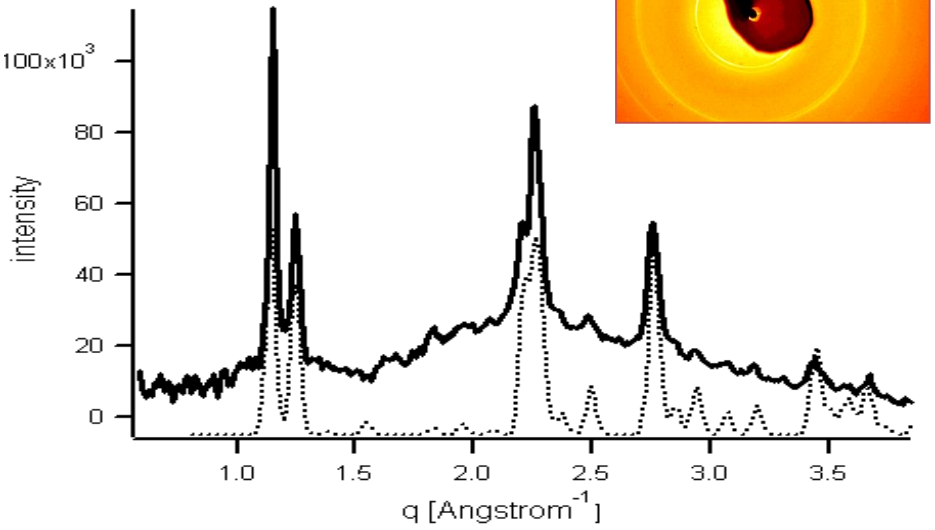
7. Bioceramics

Copper mineral in Glycera teeth

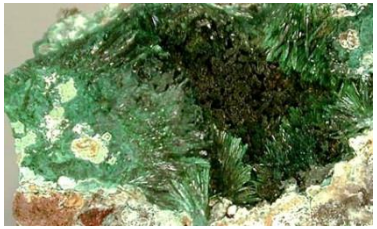
Glycera teeth were found to contain the copper mineral atacamite (copper hydroxy chloride). First copper containing biomineral found.

*Position resolved synchrotron **XRD***





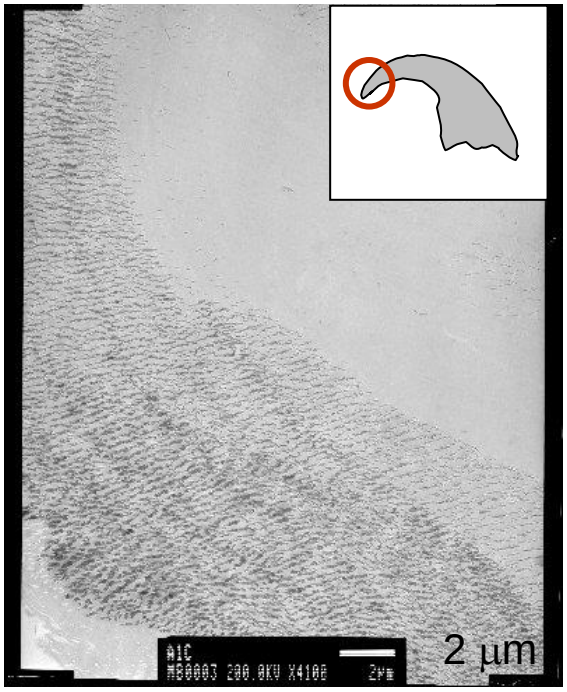
Atacamite: $Cu_2(OH)_3Cl$



7. Bioceramics

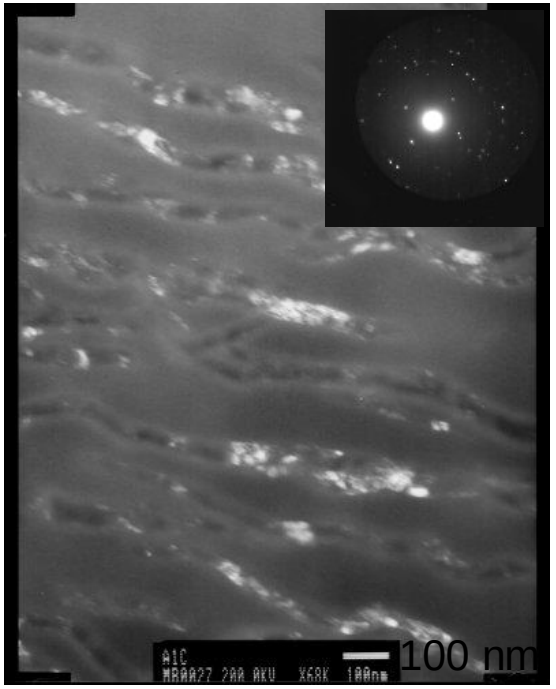
Arrangement of atacamite crystals

Transmission electron microscopy (TEM)



bright field

bright field



dark field

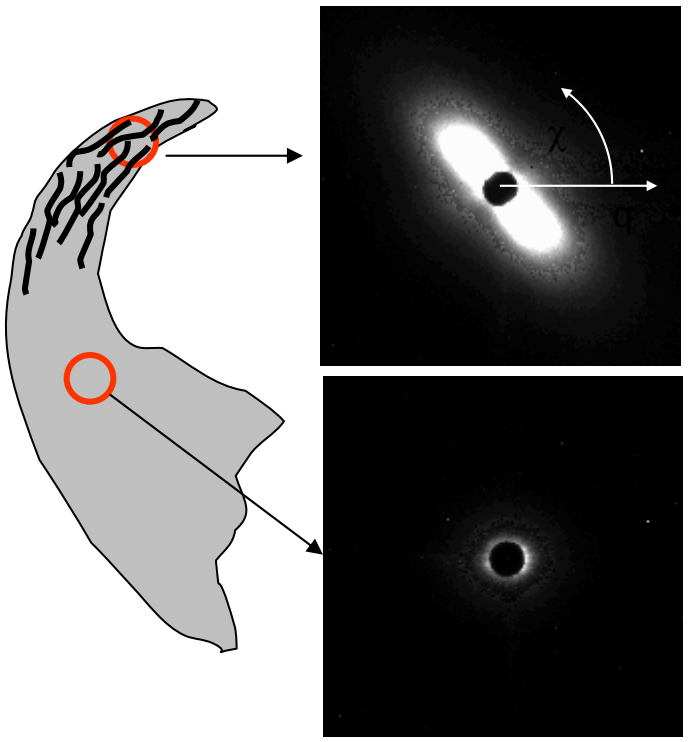
H.C. Lichtenegger, T. Schöberl, M.H. Bartl, J.H. Waite, and G.D. Stucky. *Science* 298 (5592), 389-392 (2002).

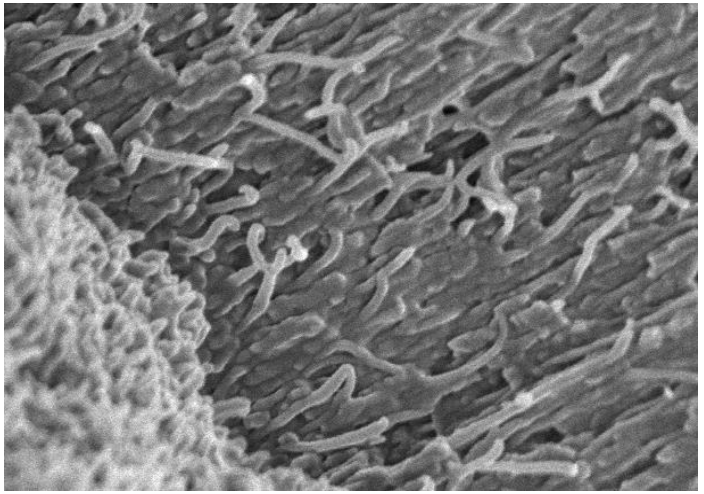
7. Bioceramics

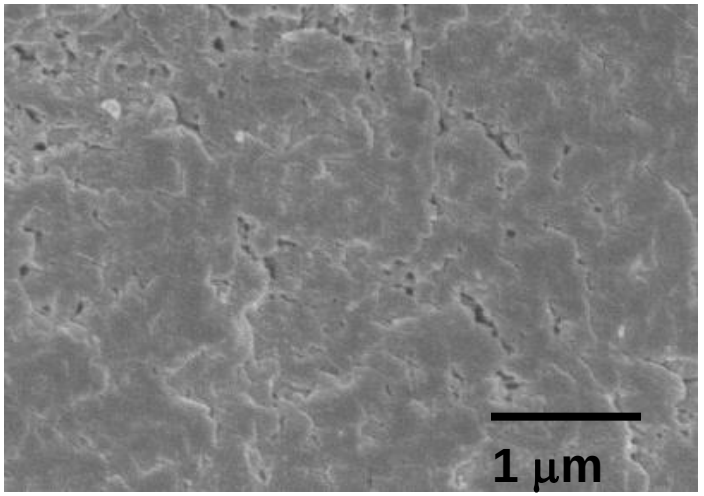
Alignment of mineralized fibers

Scanning electron microscopy (SEM)

*Synchrotron **SAXS***





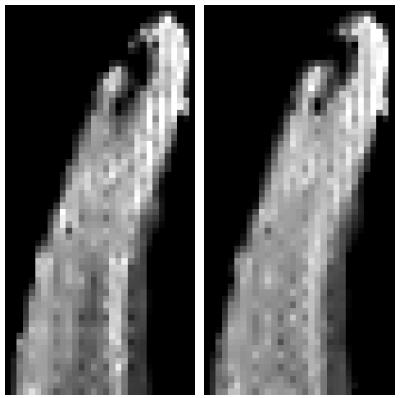


Diameter: 80 ± 15 nm.

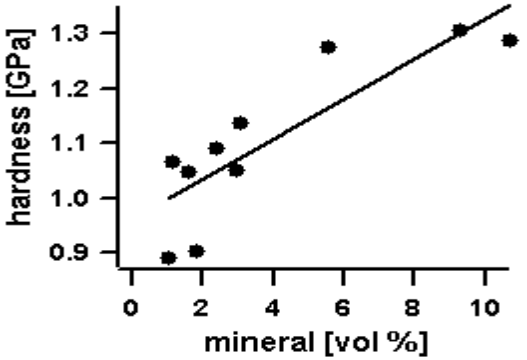
7. Bioceramics

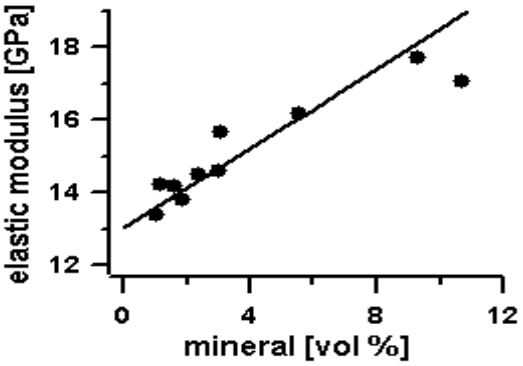
Mineral content and mechanical properties

Nanoindentation

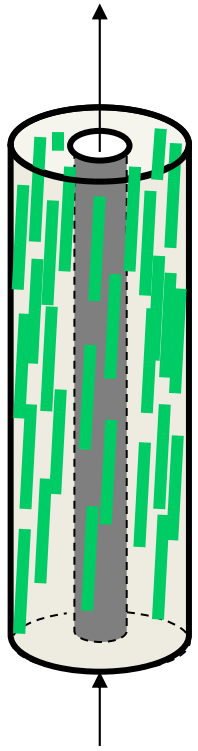


hardness stiffness



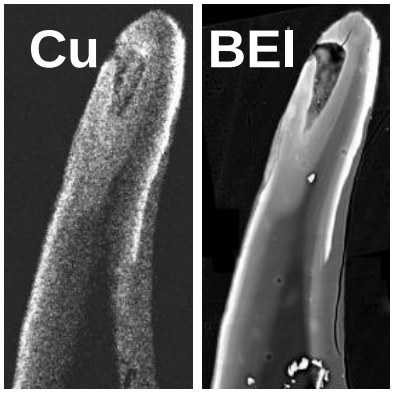


Fiber reinforced tube



venom

e^- microprobe analysis



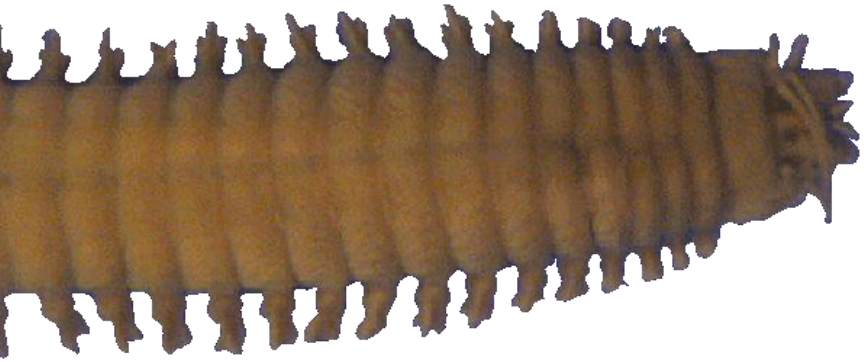
local copper concentration backscattered electron image

7. Bioceramics

Zinc in *Nereis limbata*

Nereis is a marine worm related to Glycera, but non-raptorial and equipped with teeth containing Zinc.

Zinc was found in non-mineralized form, most likely co-ordinated to the jaw protein and serving as cross-linker.



1 mm

Up to 5% Zn w/w

7. Bioceramics

Glycera live

7. Bioceramics

Summary: Bioceramics, examples of mineralized tissues

• **Nacre** (mother of pearl): consists of $CaCO_3$ tablets, stacked like coins, with thin sheath of organic glue in between -> 3000 fold increase of toughness as compared to pure calcium carbonate mineral

• **Calcitic lenses in brittlestar**: oriented with main axis in direction of entering light (avoid birefringence); shape optimized to avoid abberation in thick lens

• **Human (and vertebrate) teeth**:

dentin (inner part): similar to bone in composition (about 65% mineral)

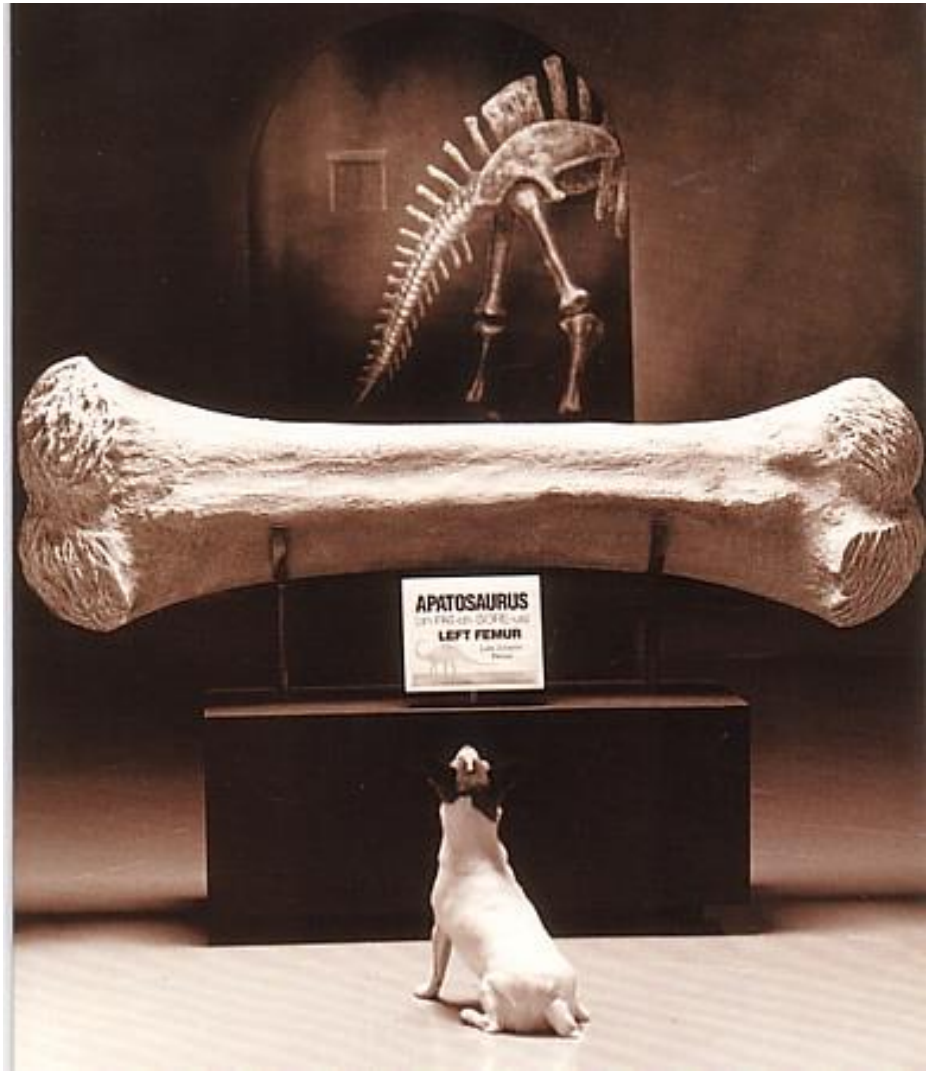
enamel (hard coating of teeth): cross running mineral rods, heavily mineralized tissue (about 95% mineral)

• **Transition metal-based teeth**:

Fe-based teeth of chitons and limpets: crystallites arranged such that a continously sharp cutting edge is ensured.

The poisonous marine worm Glycera contains copper-mineralized teeth: copper mineral atacamite embedded in dark protein matrix in form of fibers reinforcing the jaw tip

8. Bone



8. Bone

Characteristics of bone

Function

- Mechanical (protection and support)
- Metabolic (main deposit of calcium salts)

Bone is a composite material. Components:

- Protein (collagen)
- Mineral (calcium phosphate „hydroxyapatite“, $Ca_{10}(PO_4)_6(OH)_2$)
- Water

8. Bone

Material properties of bone

Table 6.4 Material properties of the major components of bone

Strength of hydroxyapatite	0.1	GPa
Stiffness of hydroxyapatite	130	GPa
Ultimate strain of hydroxyapatite	10^{-3}	
Stress in collagen at strain = 10^{-3}	1	MPa
Strength of collagen	50	MPa

Table 6.7 The importance of the organic phase to the mechanical properties of bone

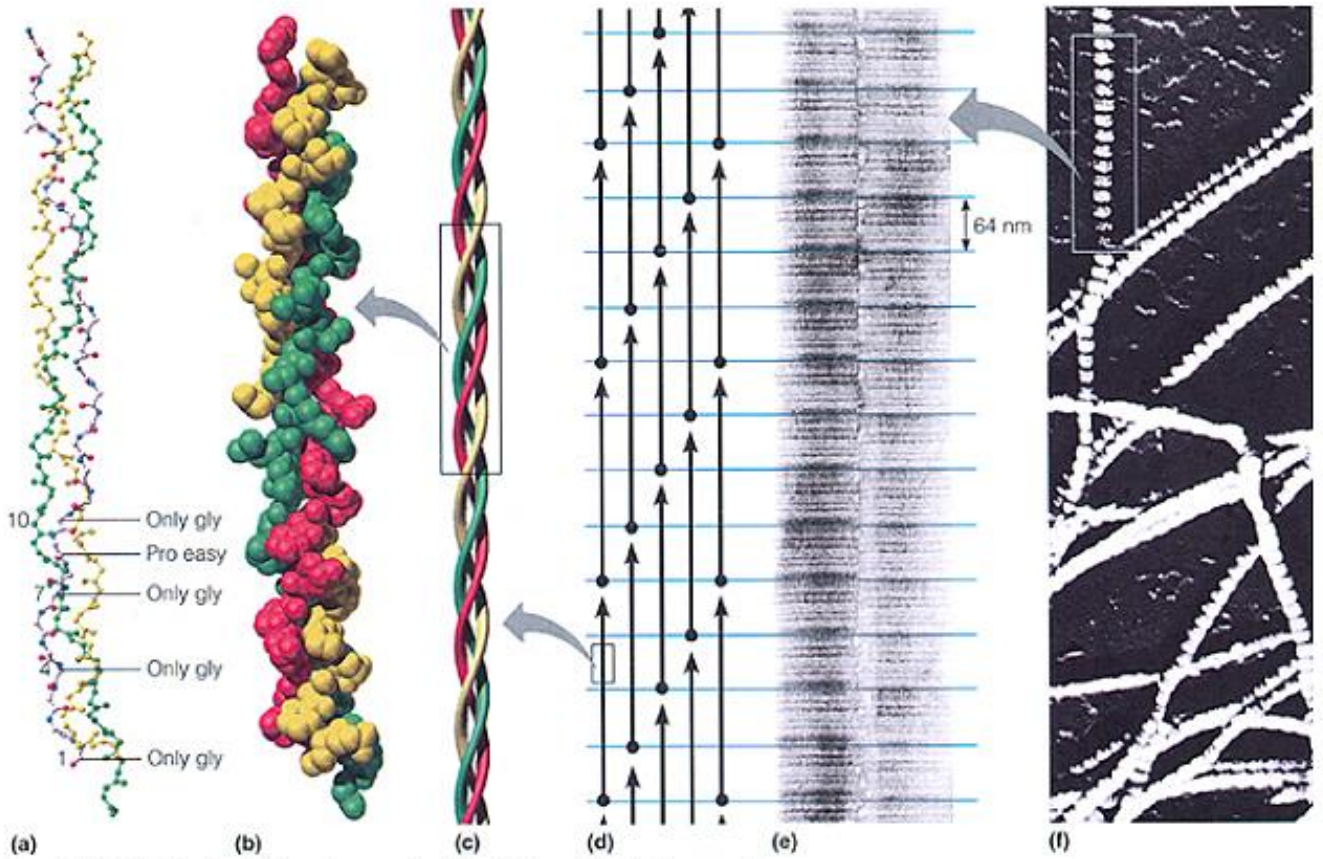
	Tension		Compression	
	Strength (MPa)	*E* (GPa)	Strength (MPa)	*E* (GPa)
Normal	130	17	150	9
Organic phase removed	6	17	40	7.2

8. Bone

Collagen

Structural fibrous protein, remember structrure:

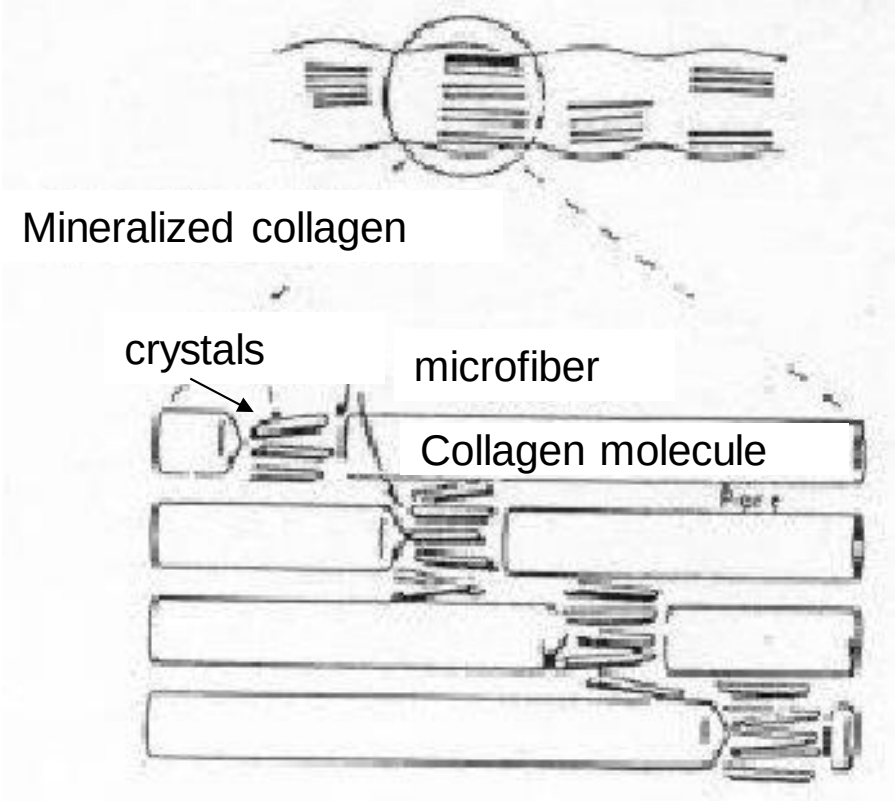
Amino acid sequence: (Gly-X-Y)n, triple helix, staggered molecule arangement with gap-overlap zones



8. Bone

Bone mineralization

Mineralization starts in spaces in between collagen molecules (gap zones).

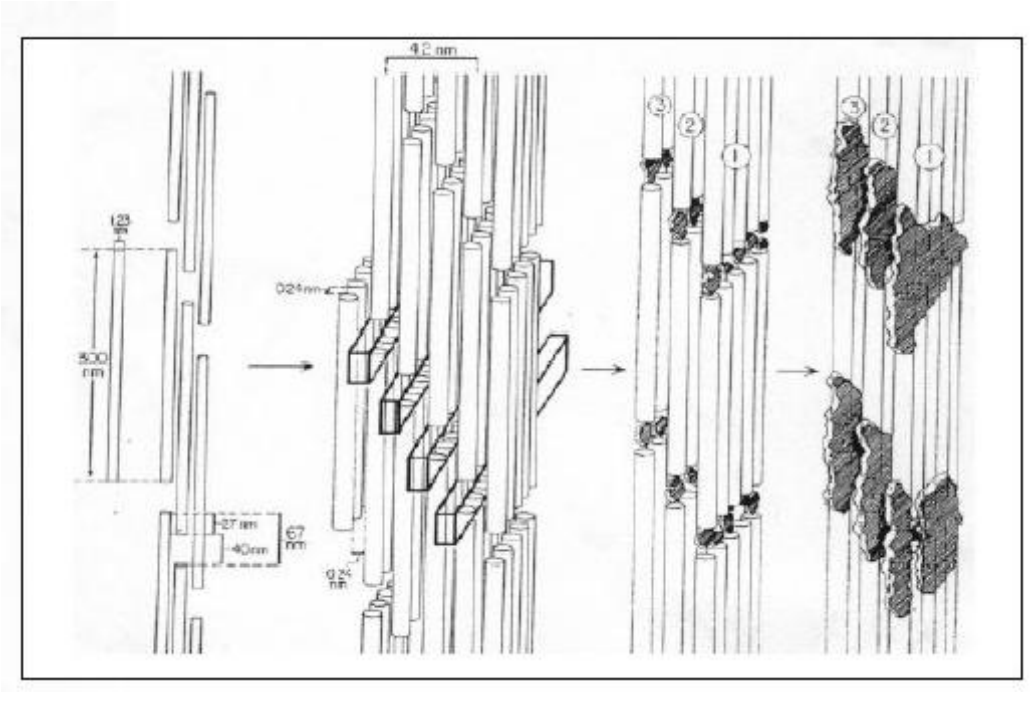


8. Bone

Bone mineralization

Crystals get larger, eventually grow out of gap in between collagen molecules.

Size of mineral crystallites: plates 50x25x2 nm (belong to the smallest objects produced in biological process), bone is a nanocomposite material



„Hodge-Petruska model“

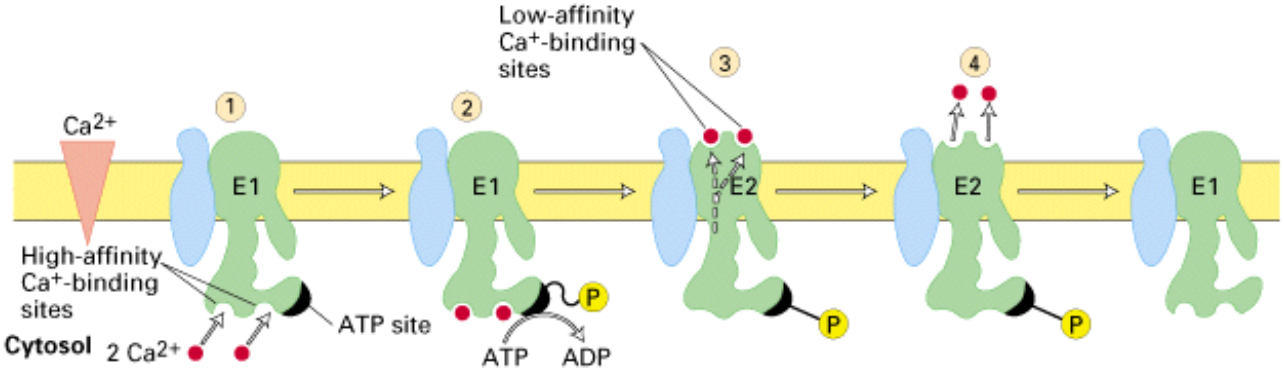
c-axis
of HAP

8. Bone

Role of calcium in metabolism

Ca ions can can bind to adenosine triphosphaste (ATP), is expelled from the cell to lower the concentration of Ca in the cellular fluid (10^{-7} as compared to 10^{-3} M in extracellular fluids)

-> small changes in Ca concentration can be used for **signalling purposes**

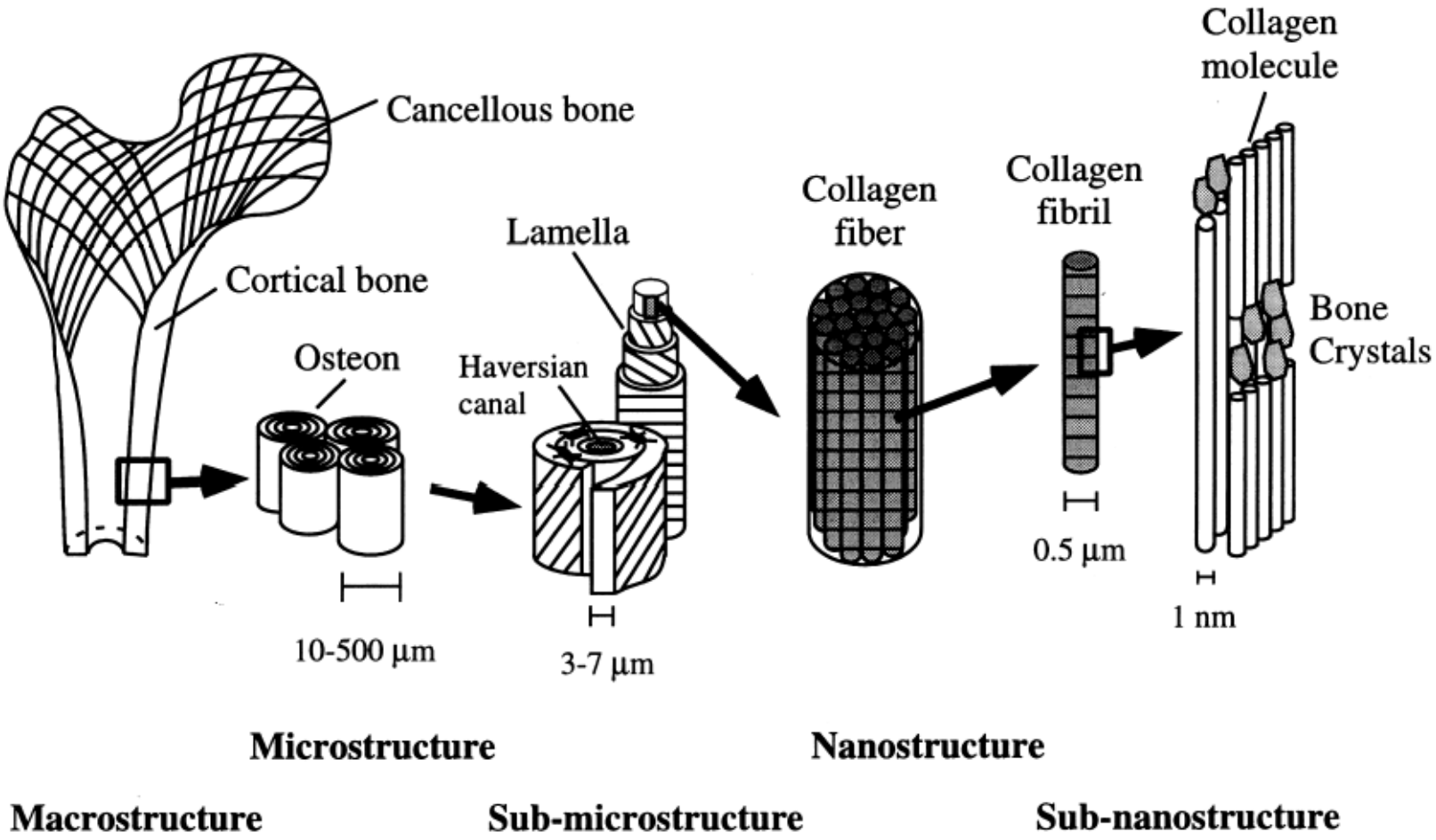


Transport of Ca ions across membrane (out of cell, or into cellular vesicle, where mineralization may take place)

8. Bone

Hierarchical structure of bone

Different structures and morphologies on different length scales:



8. Bone

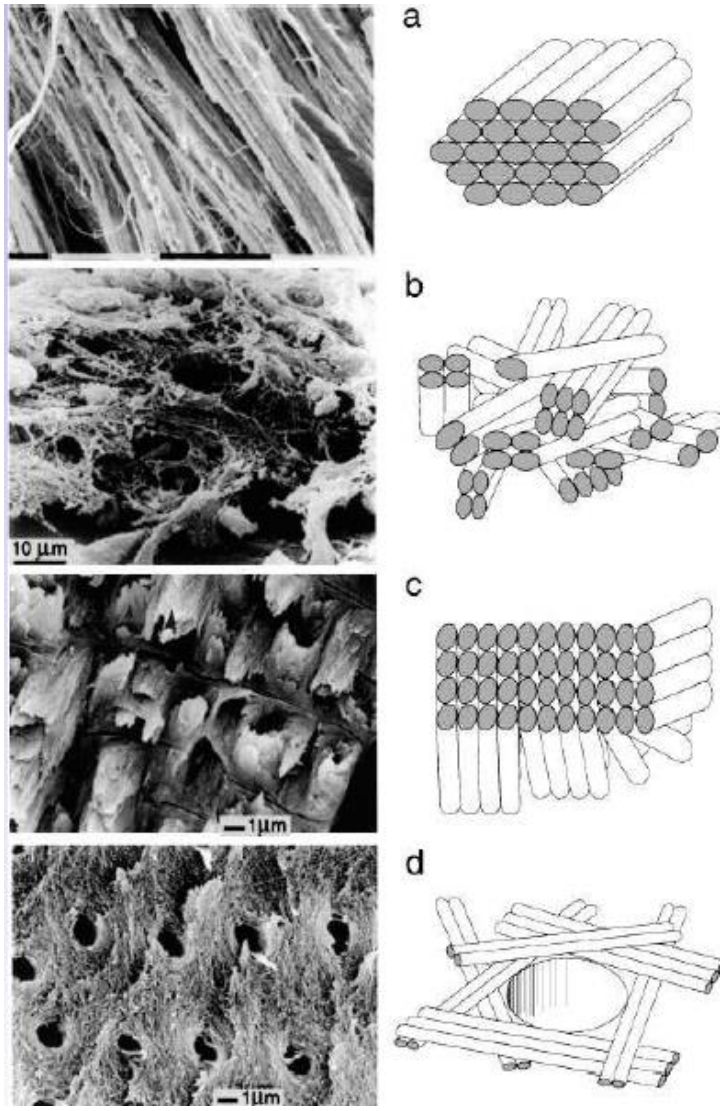
Fiber arrangement bone

parallel fibers

woven bone
(weak, laid down first
during wound healing)

lamellar bone
(„normal“ bone)

radial arrangement
(dentin)



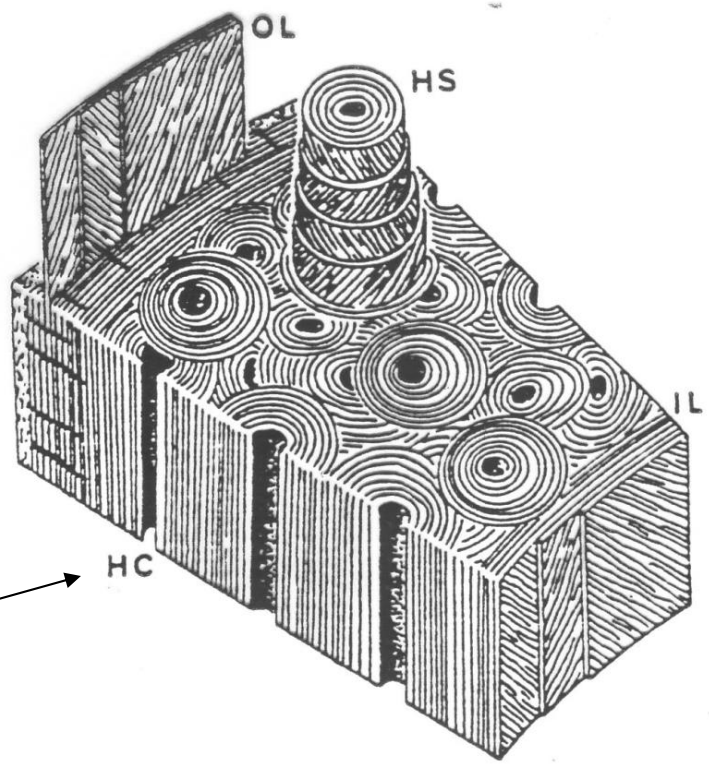
8. Bone

Osteons

Structural element of bone found in compact bone.

Hole in the middle: haversian canal, contains blood vessels.

Mineralized collagen fibers are wound around osteon in concentric layers, with collagen oriented in a spiral-like way in each of the layers and orientation at different angles in different layers.



Haversian canal

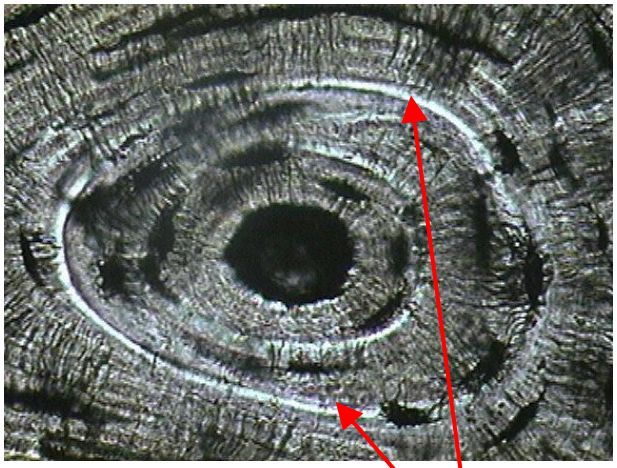
8. Bone

Osteons

Growth of bone: starts from inside the osteon, in layers.

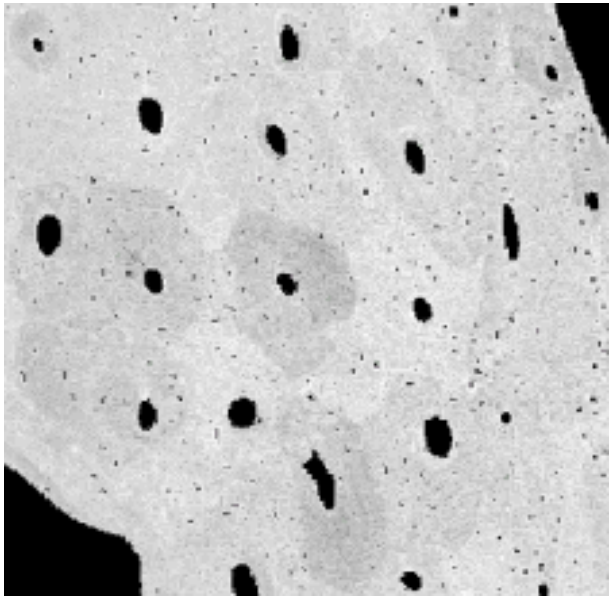
Primary osteon: newly formed in growing bone

Secondary osteon: result of bone remodeling (resorption and re-deposition of bone starting), surrounded by cement layer containing very little collagen



Secondary osteon

Cement layer



Osteons in compact bone.

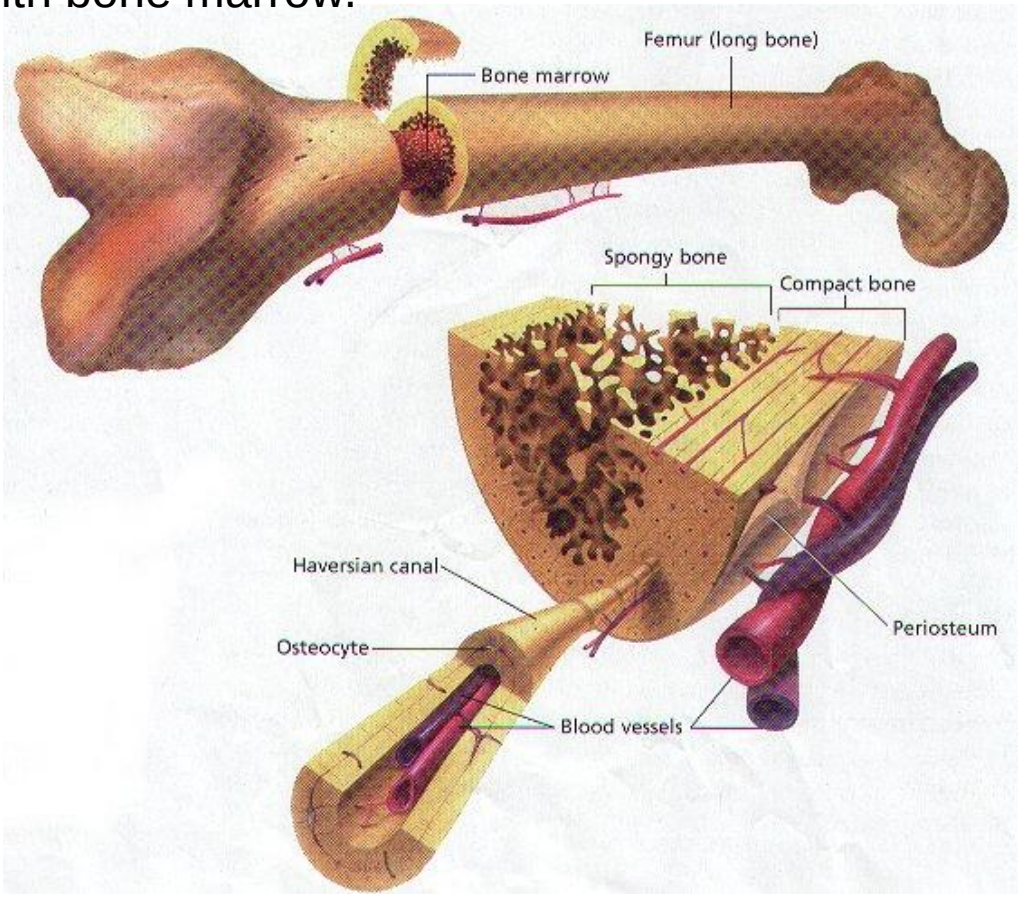
Normal compact bone = lamellar bone

8. Bone

Compact bone, spongy bone

Compact bone (Corticalis): found in long bone, and generally outer layer of bone, contains osteons

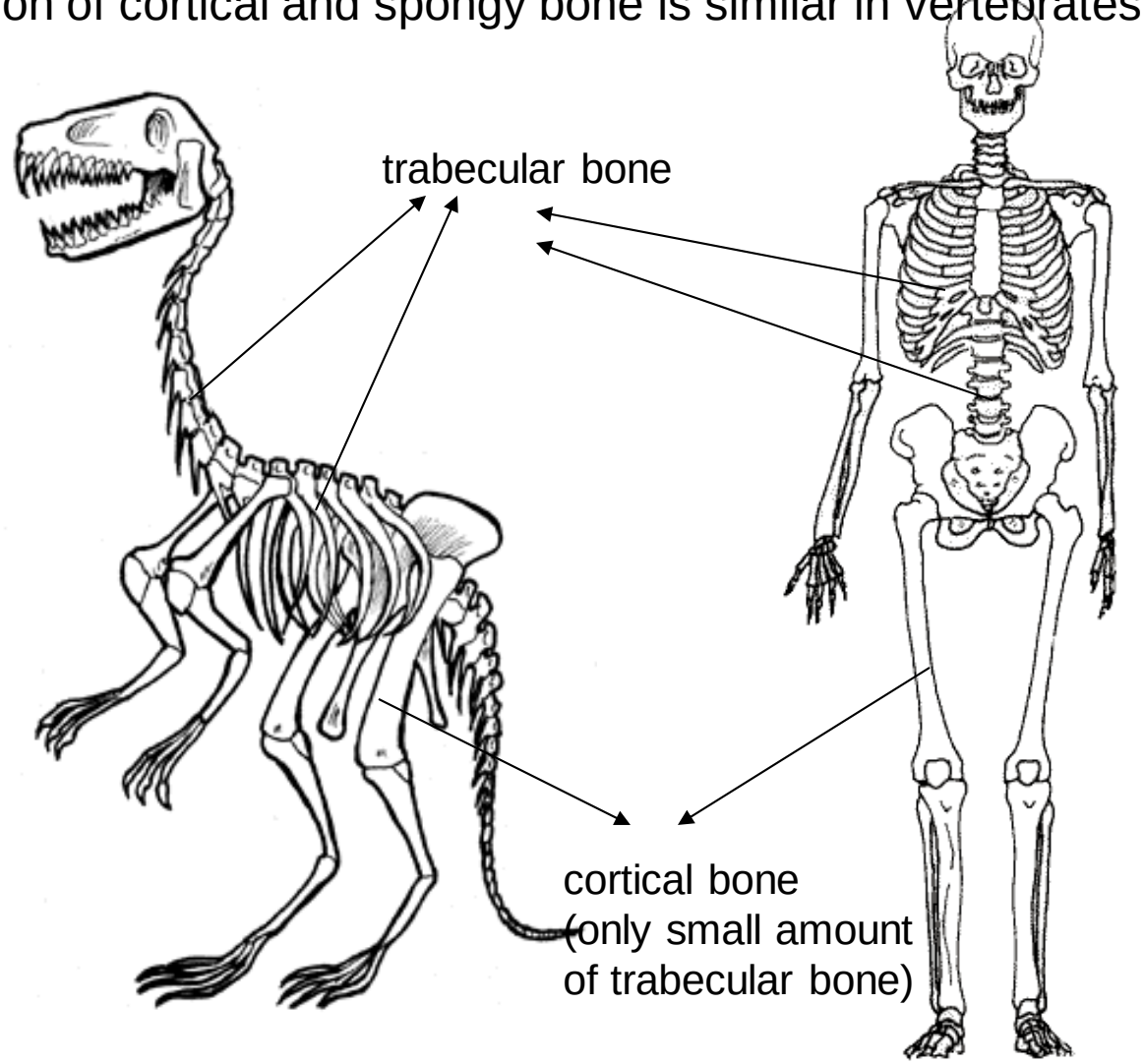
Spongy bone (Spongiosa): sponge like bone filling the inside of bones, spaces in between filled with bone marrow.



8. Bone

Spongiosa - corticalis

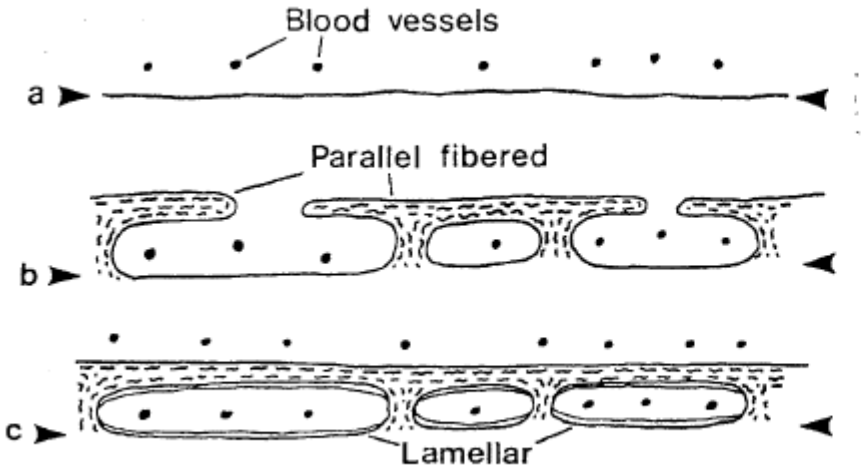
Distribution of cortical and spongy bone is similar in vertebrates

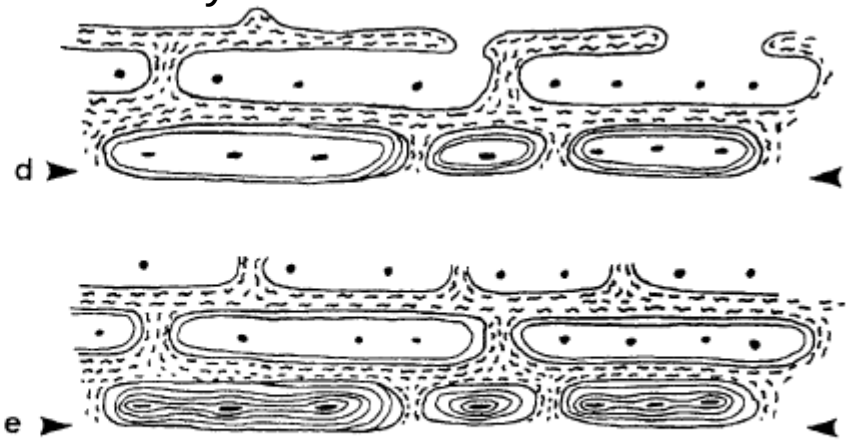


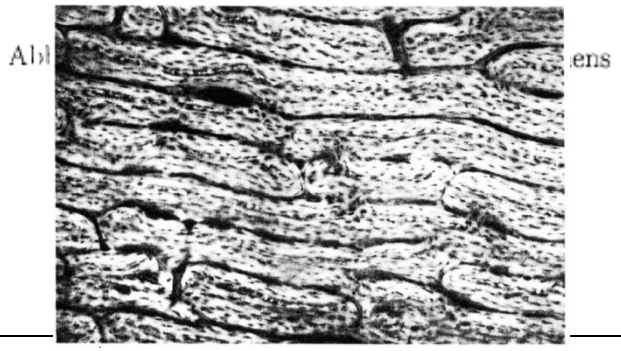
8. Bone

Fibrolamellar bone

Dense bone type formed in fast-growing and heavy animals.







Heaviliy mineralized, very few blood vessels.

Did you know that:
horses are usually shot when they break a leg?
The corticalis of their legs (as in ungulates in general) has almost no secondary osteons (fibrolamellar bone), blood supply is limited, fractures heal very slowly.

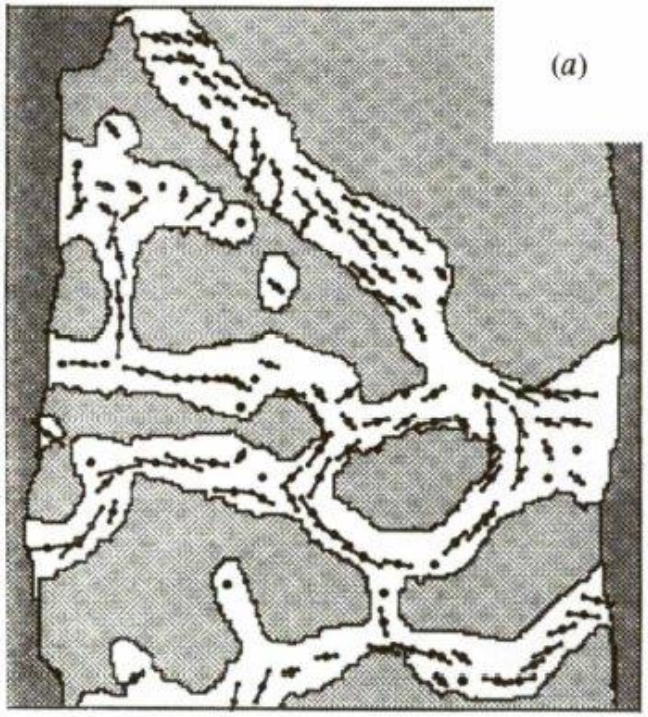
8. Bone

Spongiosa (spongy bone, trabecular bone)

Fills the inside of long bones.

Network of bone trabeculae with spaces in between. Trabeculae tend to follow directions of principal stresses in bone (light weight structure).

Thickness of trabeculae: approx. 200 μm.



Orientation of mineral particles (and collagen fibers) along the direction of the trabeculae.

8. Bone

Bone cells

Osteoblasts: make bone. Found on the surface, produce non mineralized collagen fibers.

Later on become trapped inside the bone, turn into osteocytes

Osteoclasts: responsible for resorbing bone

Start by dissolving mineral (in acid), then resorb collagen molecules).

Holes are filled again by osteoblasts between old and new bone layer of so-called cement.

Osteocytes: osteoblasts trapped in lacunae inside bone, task not exactly known, maybe act as sensors for external stresses and may direct adaptive growth

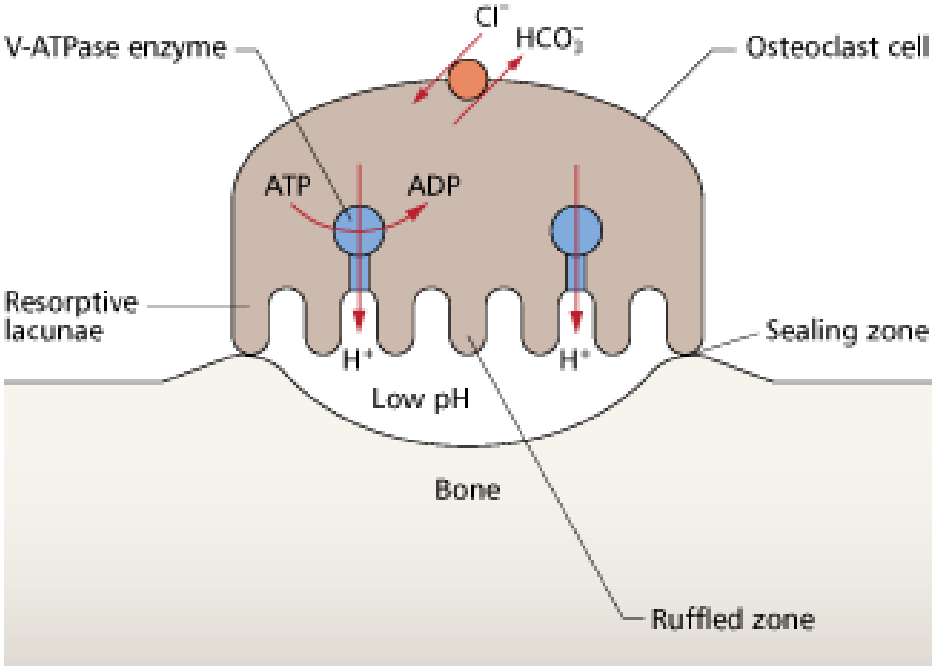
8. Bone

Bone remodeling

Bone resorption by Osteoclasts:

Osteoclasts are large cells, attach to bone surface, seal off interface.

First HAP mineral is dissolved in acid, then collagen is enzymatially digested.

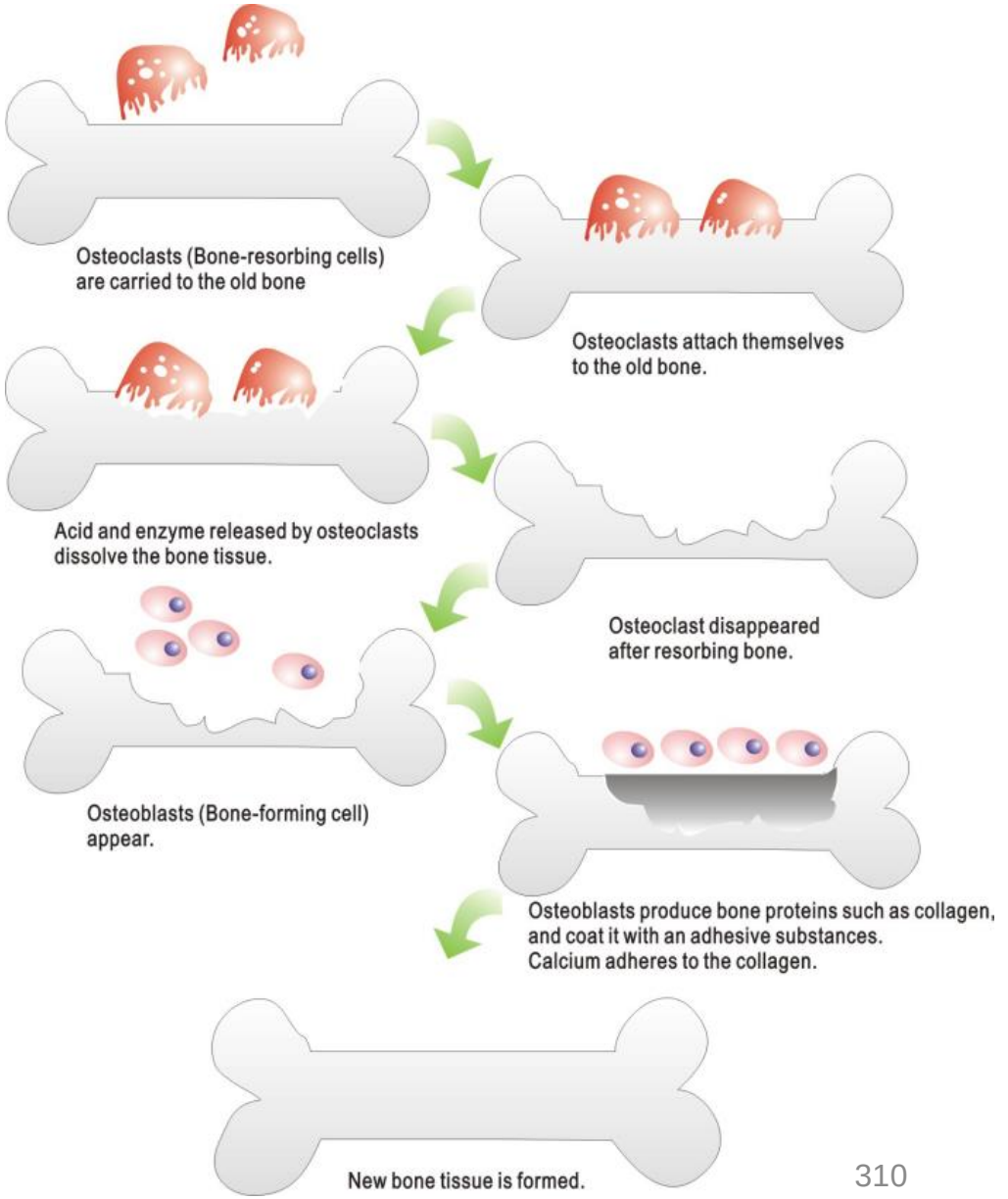


8. Bone

Bone remodeling

Bone resorption by osteoclasts is followed by deposition of collagen by osteoblasts.

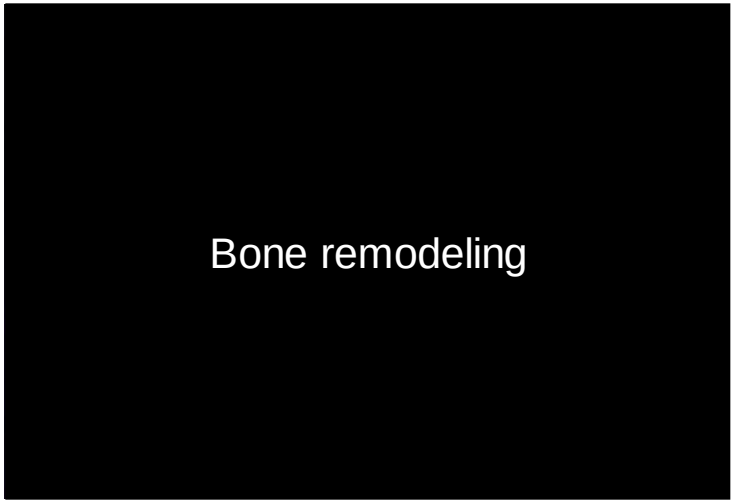
Newly formed collagen is then mineralized.



8. Bone

Bone remodeling movie

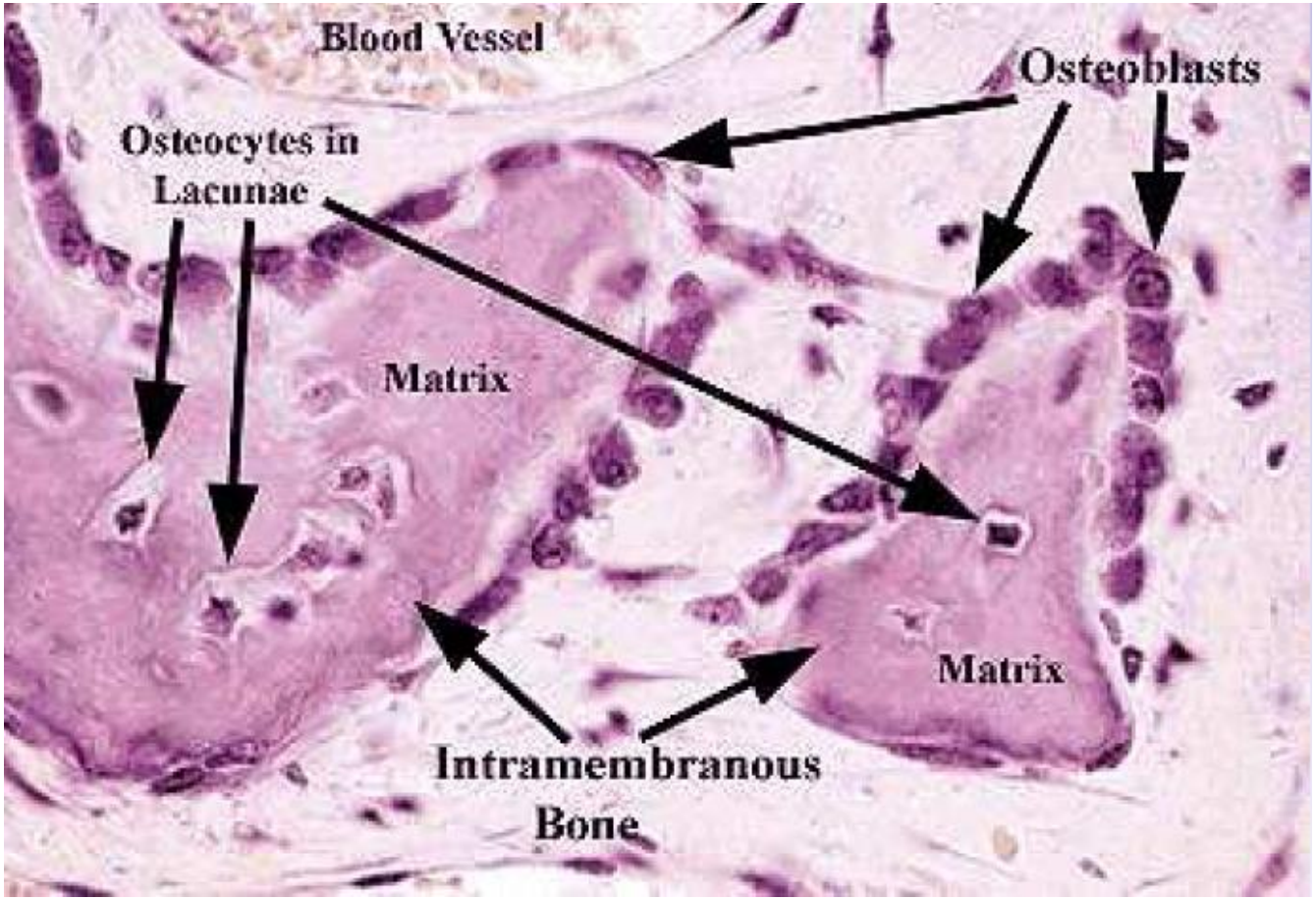
.



8. Bone

Bone cells under the microscope

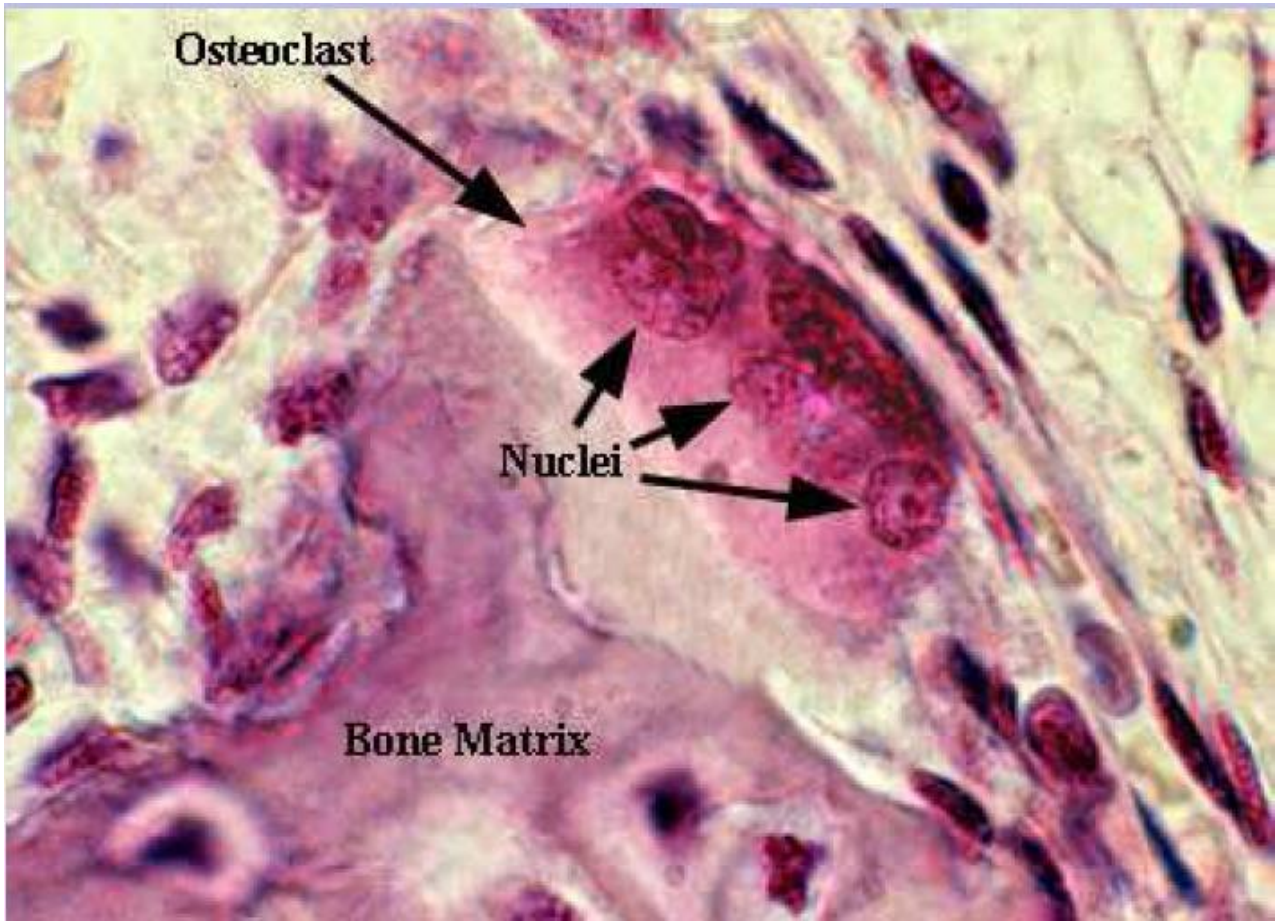
Forming of new bone by Osteoblasts



8. Bone

Bone cells under the microscope

Bone resorption by osteoclasts



8. Bone

Mechanical properties of bone

Mechanical properties depend on moisture:

Dry bone fractures in brittle way, wet bone can be deformed plastically.

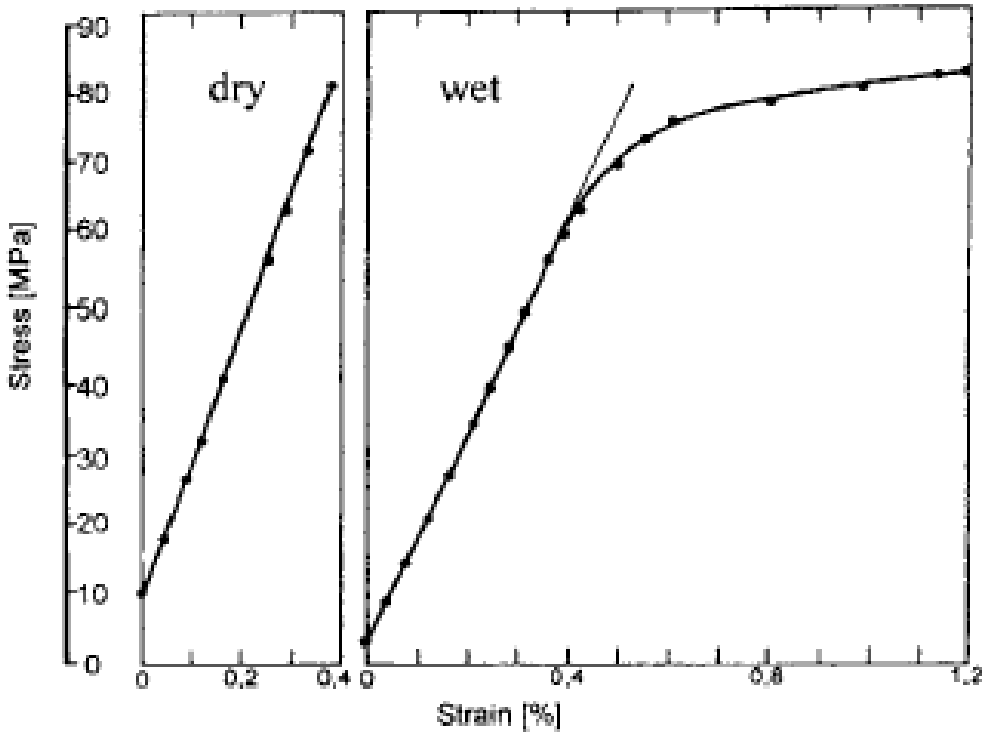


Fig. 3.10. Effect of humidity on the stress-strain curve of human femur. Adapted from Evans and Lebow (1951).

8. Bone

Mechanical properties of bone

Bone is highly viscoelastic :

becomes stronger at higher deformation rates.

„Normal“ working conditions for bone: deformation rate of 0.001/s for slow walking, 0.01/s for more intense activity.

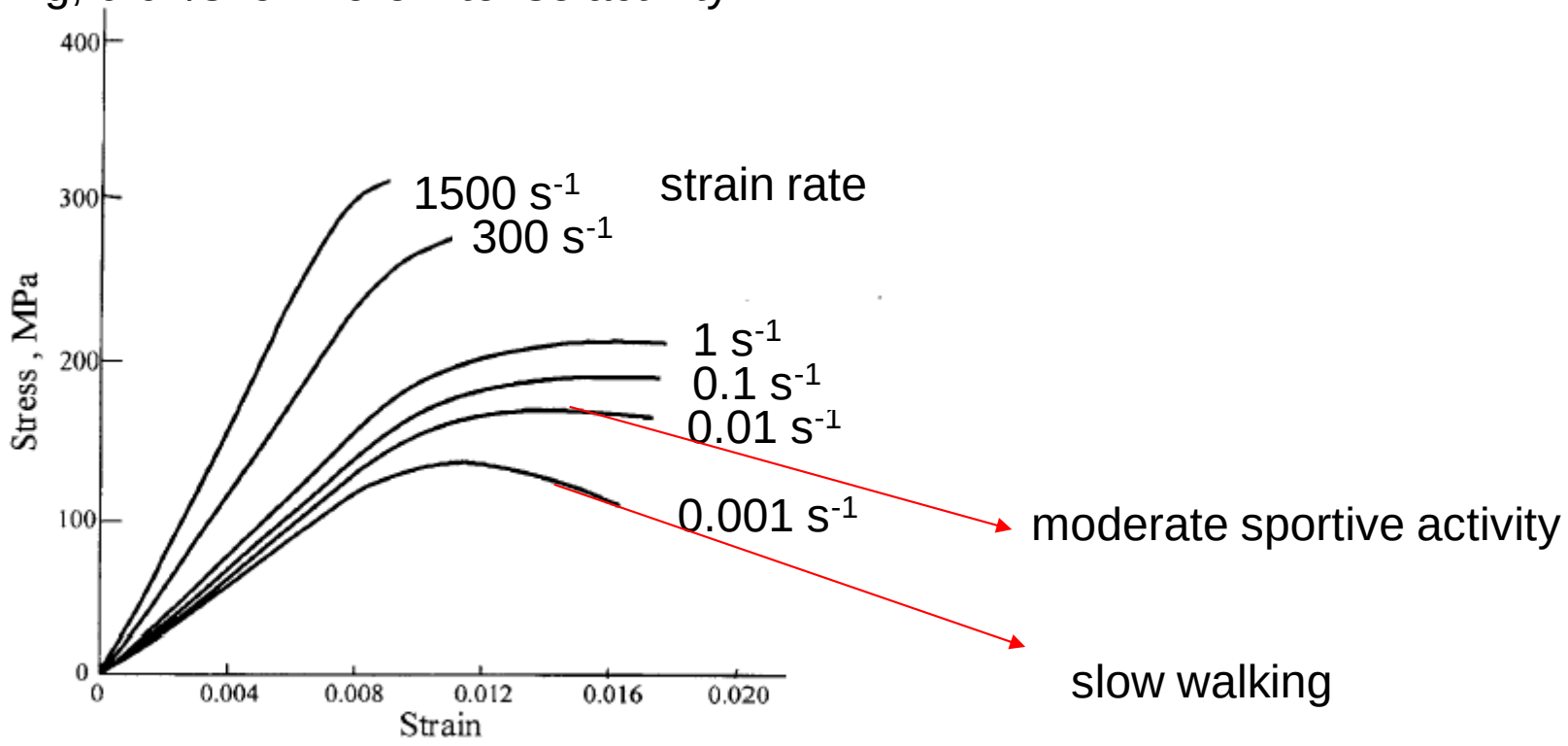


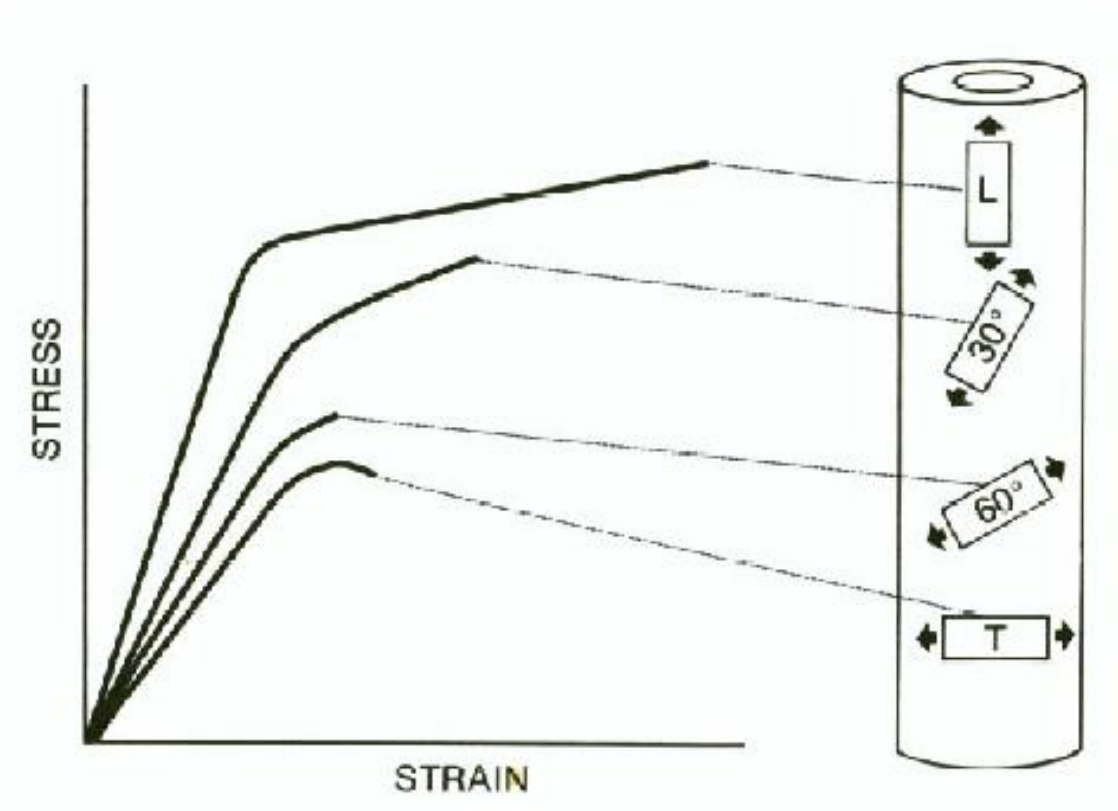
Fig. 3.8. Influence of strain-rate on the stress-strain behaviour in bone. Adapted from McElhaney (1966).

8. Bone

Mechanical properties of bone

Bone is mechanically anisotropic:

Strongest in longitudinal direction, weakest in transverse direction.

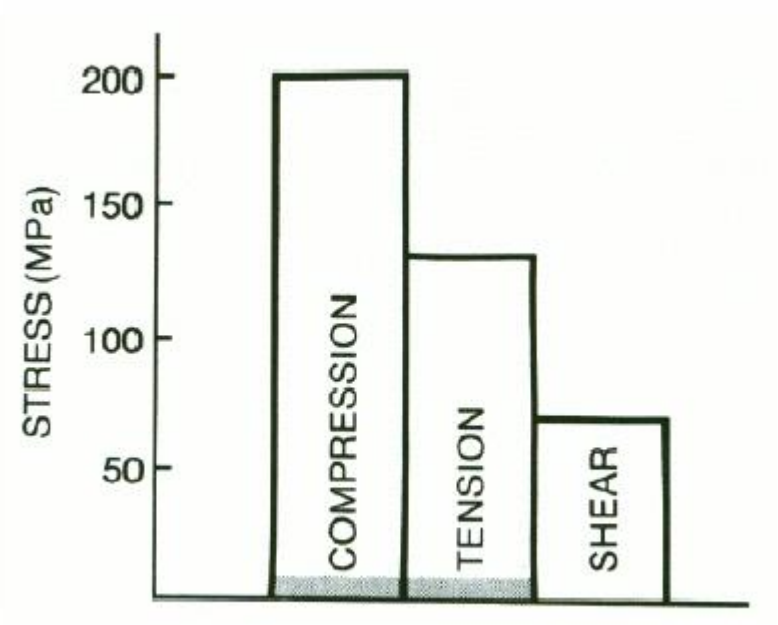


8. Bone

Mechanical properties of bone

Depend on the loading mode:

Highest strength in compression, medium in tension, lowest in shear.

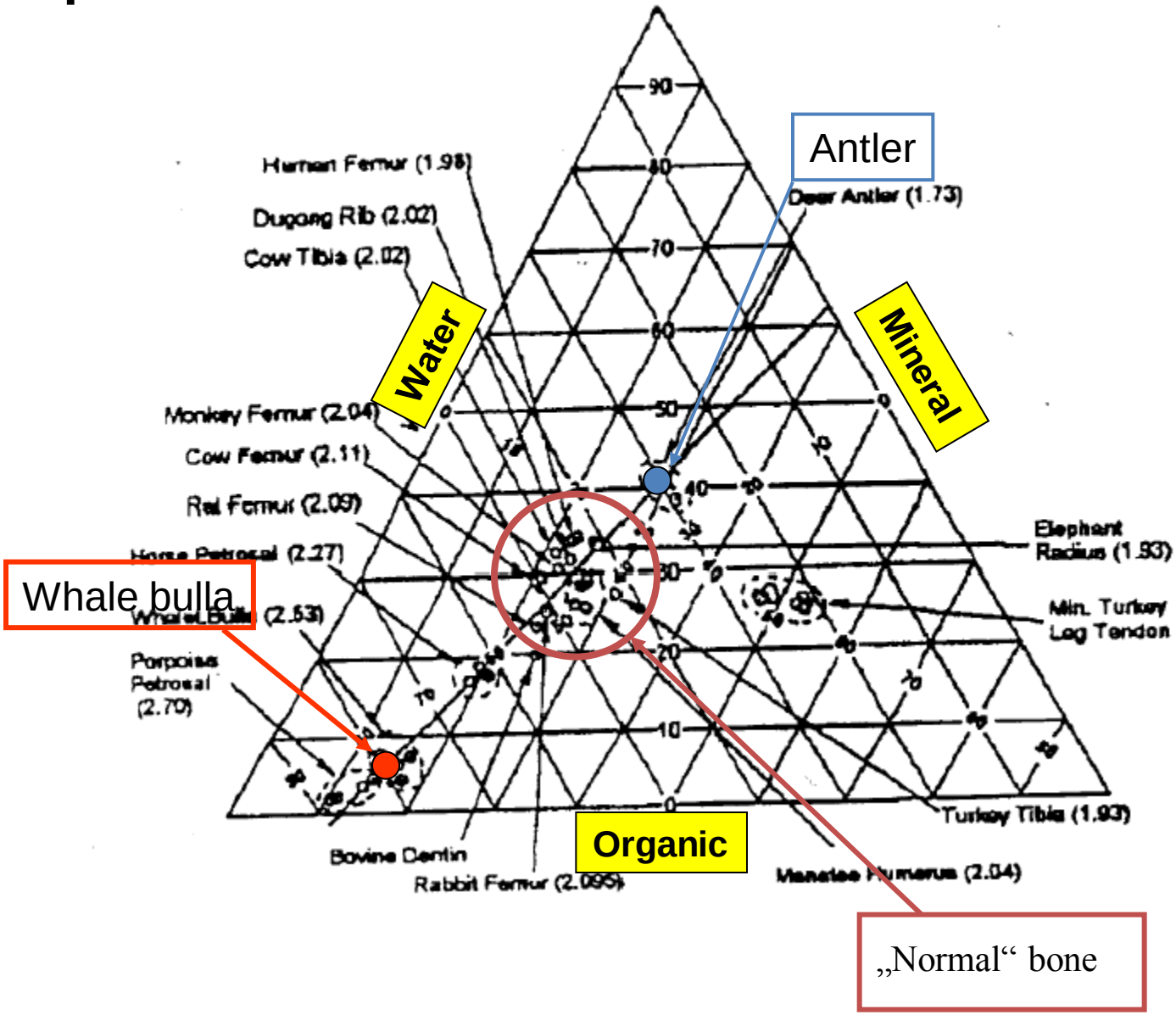


Stiffness dependence on loading mode:

Modulus of femoral cortical Bone	
Longitudinal	17.0 GPa
Transverse	11.5 GPa
Shear	3.3 GPA

8. Bone

Composition of various kinds of bone

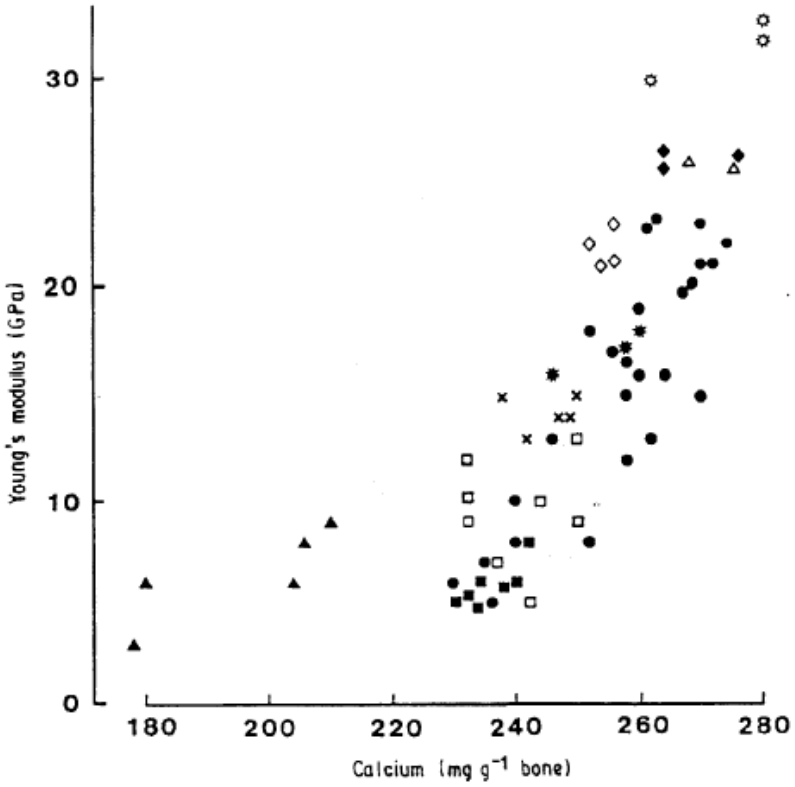


8. Bone

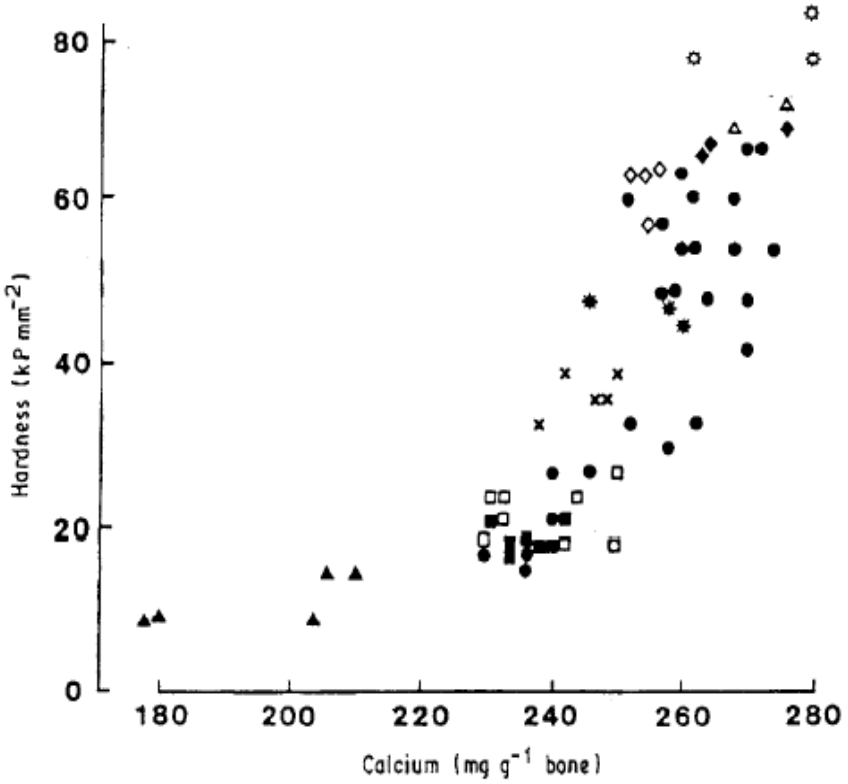
Influence of mineralization

Increasing degree of mineralization → increasing hardness and stiffness

stiffness



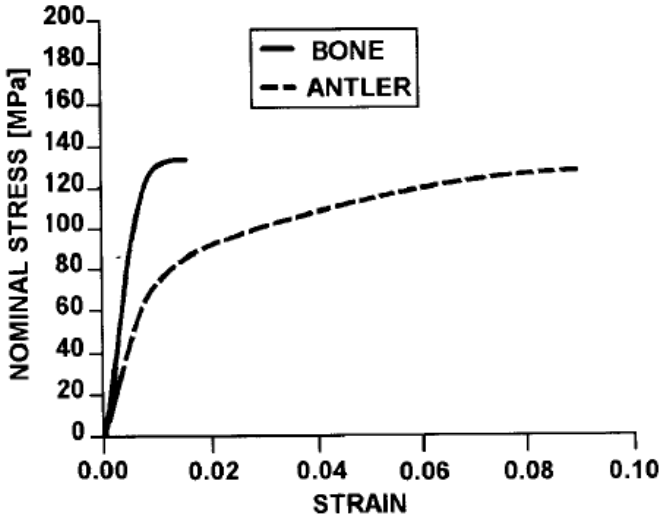
hardness



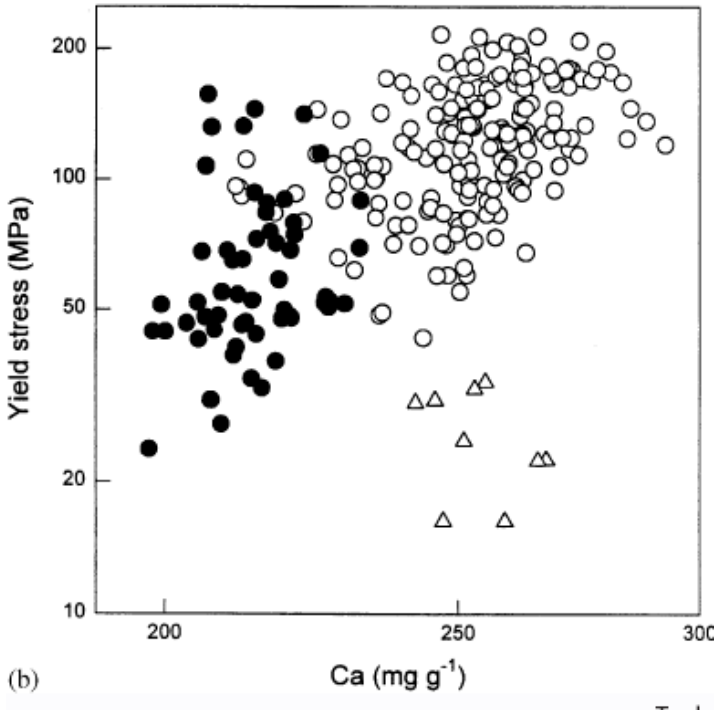
8. Bone

Influence of mineralization

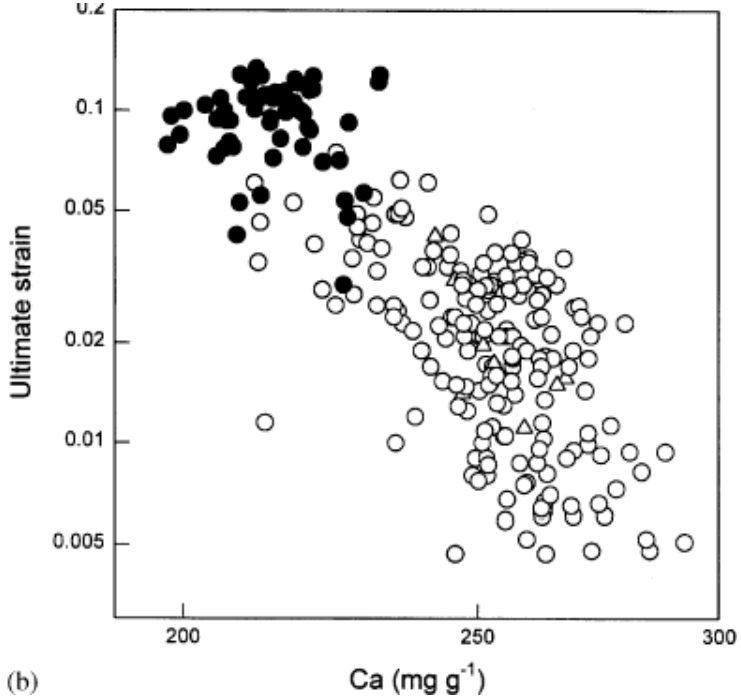
Plasticity and toughness decrease with increasing degree of mineralization.



Yield stress



Ultimate strain

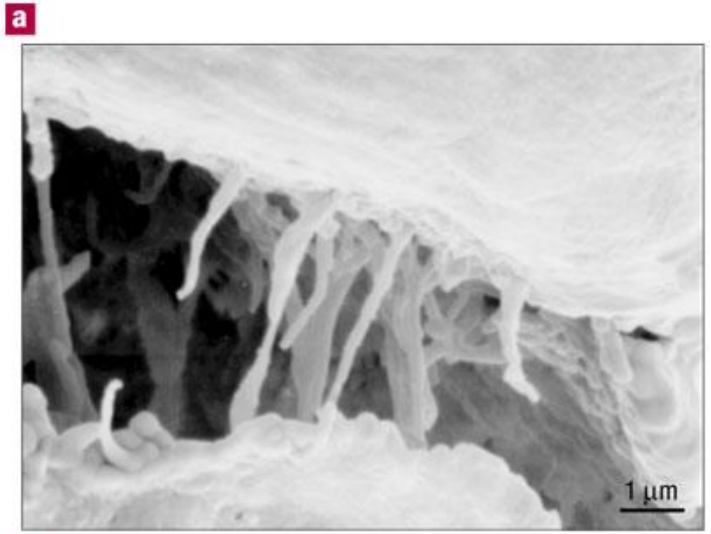


Black symbols: antler

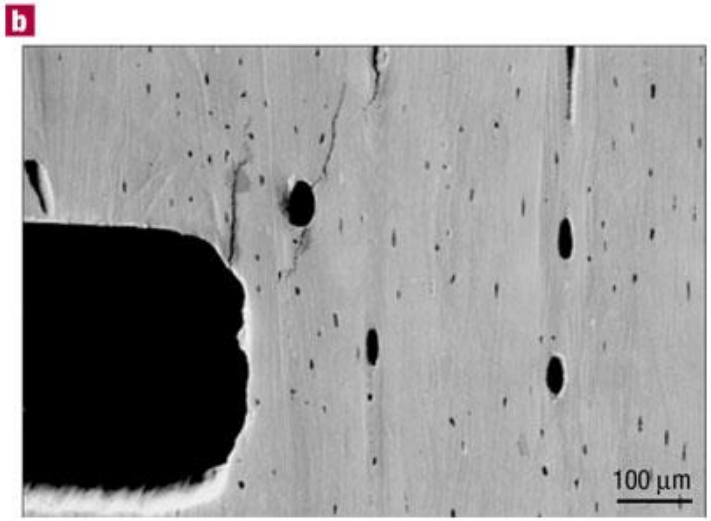
8. Bone

Fracture of bone

Toughening mechanisms:



Bridging of cracks by collagen fibers

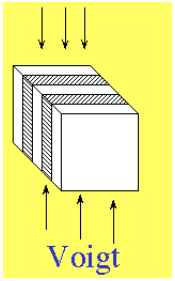


Introduction of secondary cracks

8. Bone

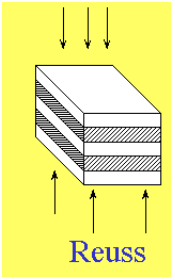
Composite behavior

Voigt:



$$\frac{1}{E} = \frac{V_1}{E_1} + \frac{1-V_1}{E_2}$$

Reuss:

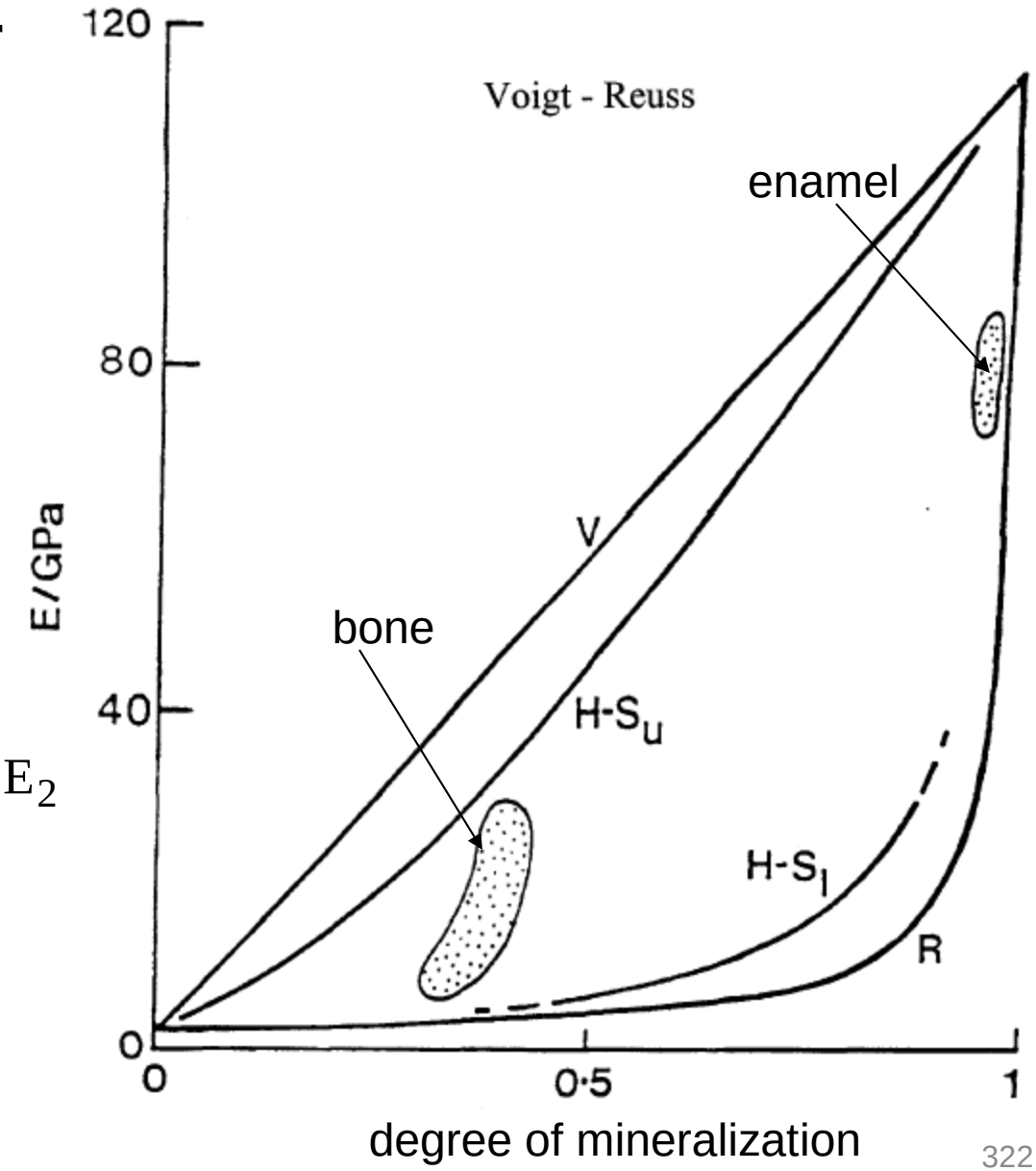


$$E = V_1 E_1 + (1-V_1) E_2$$

Other mechanical models:

Hashin-Shtrikman (H-S)

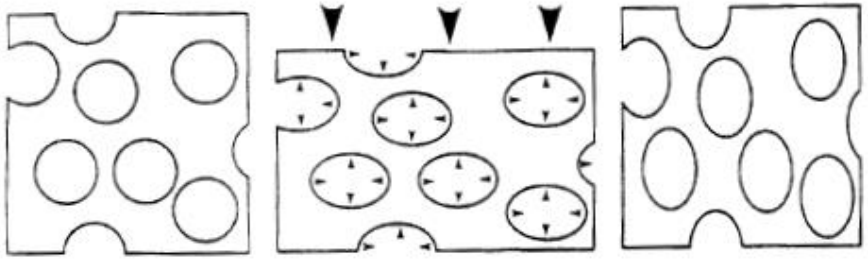
Halpin-Tsai



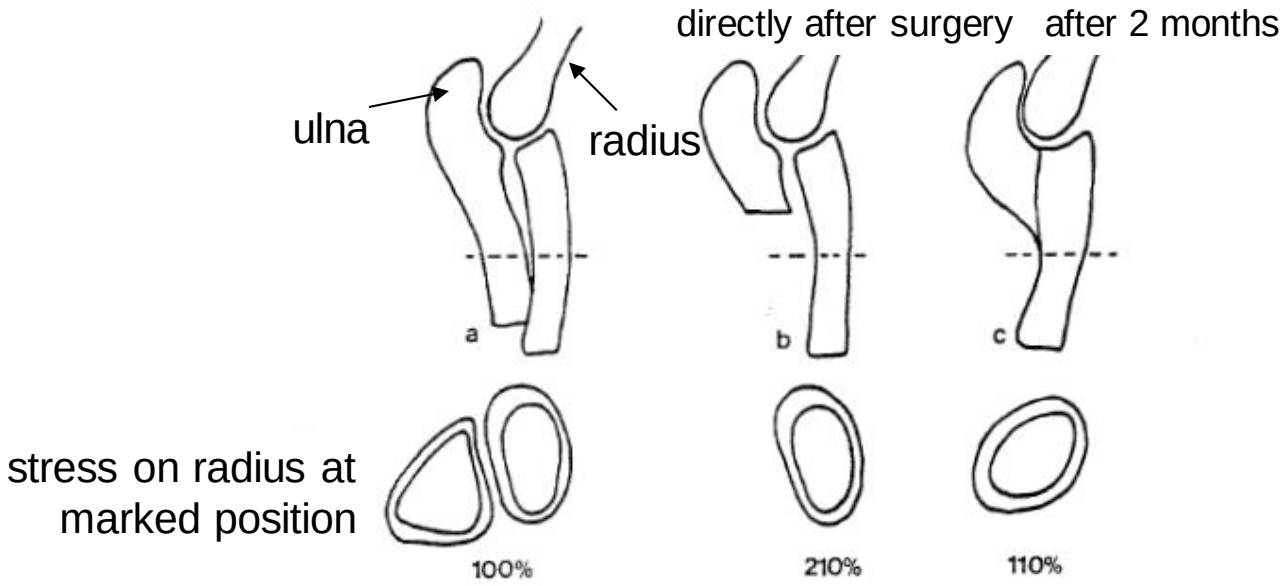
8. Bone

Adaptive growth of bone

Schematic for remodeling trabecular bone structure



Macroscopic shape remodeling after ulna removal in pig

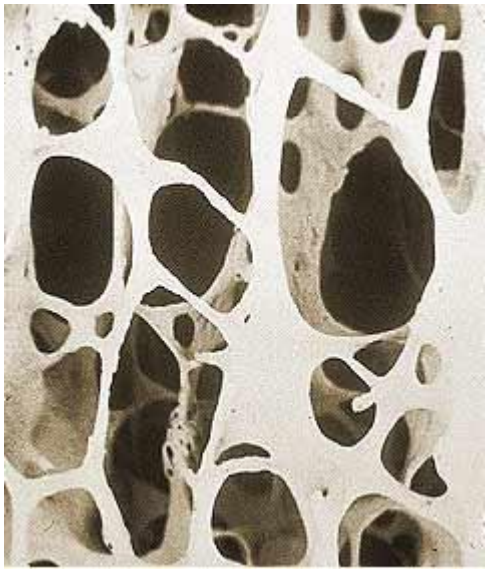


8. Bone

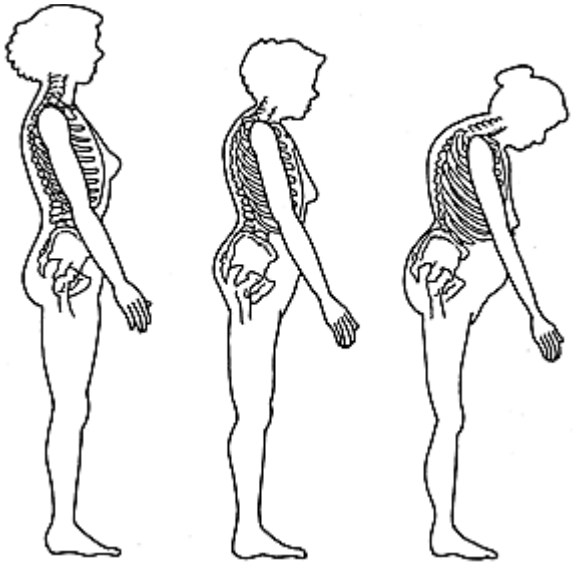
Osteoporosis

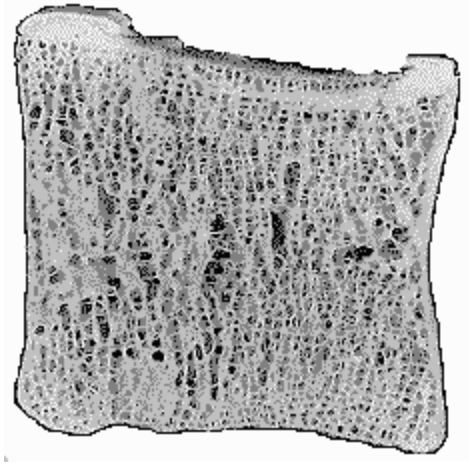
More bone resorption than redeposition.

Decrease of bone density and decrease of trabecular thickness in spongy bone.

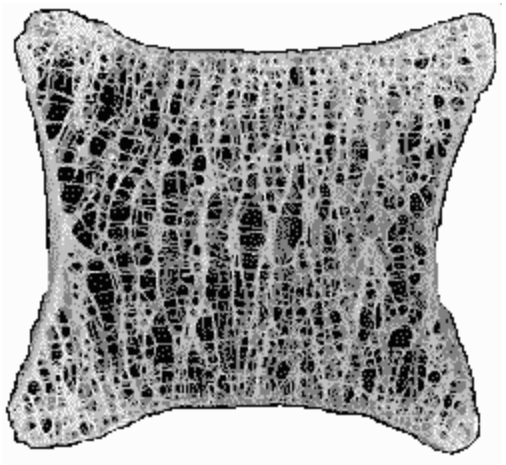


Age: 45 65 85





healthy



osteoporotic

8. Bone

Osteogenesis imperfecta

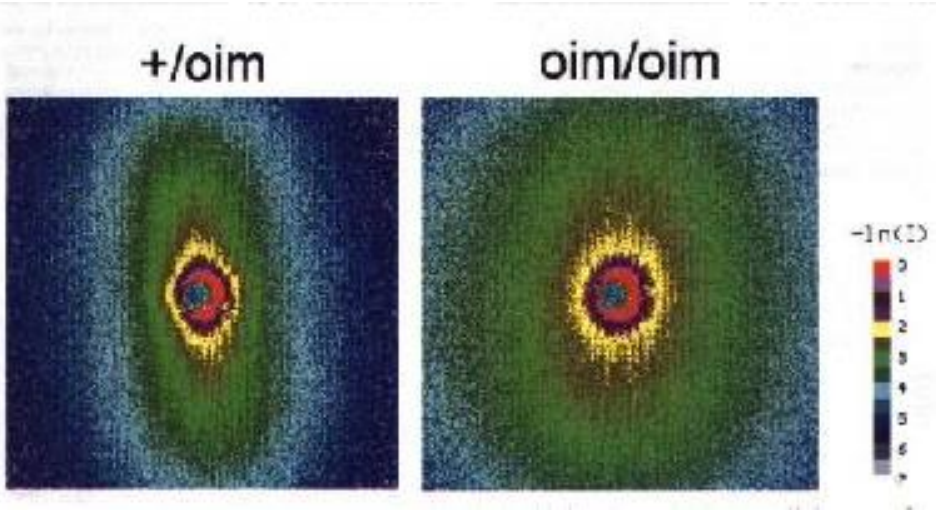
Genetic disorder characterized by bones that break easily, often from little or no apparent cause.

OI is caused by a genetic defect that affects production of collagen.

In OI, a person has either less collagen than normal, or a poorer quality of collagen* than normal--leading to weak bones that fracture easily.

OI also affects mineral orientation in bone

normal OI



Small-angle x-ray scattering images reflecting orientation distribution of mineral / collagen.
P. Fratzl et al.(1996) *J. Clin. Invest.* **97**(2): 396-402

*normal bone: 2 α_1 + 1 α_2 – chains of collagen -> 2 telopeptide ends per triple helix

oi-bone: 3 α_1 – chains -> 3 telopeptide ends per triple helix

8. Bone

Summary Bone

Bone is a composite material of collagen and hydroxyapatite mineral; efficient combination of organic and inorganic: strength of bone (130 MPa) higher than strength of both components (collagen 50 MPa, HAP 100 MPa)

The structure of bone is strictly hierarchical: nanocomposite, lamellar structure, osteons, trabecular structure

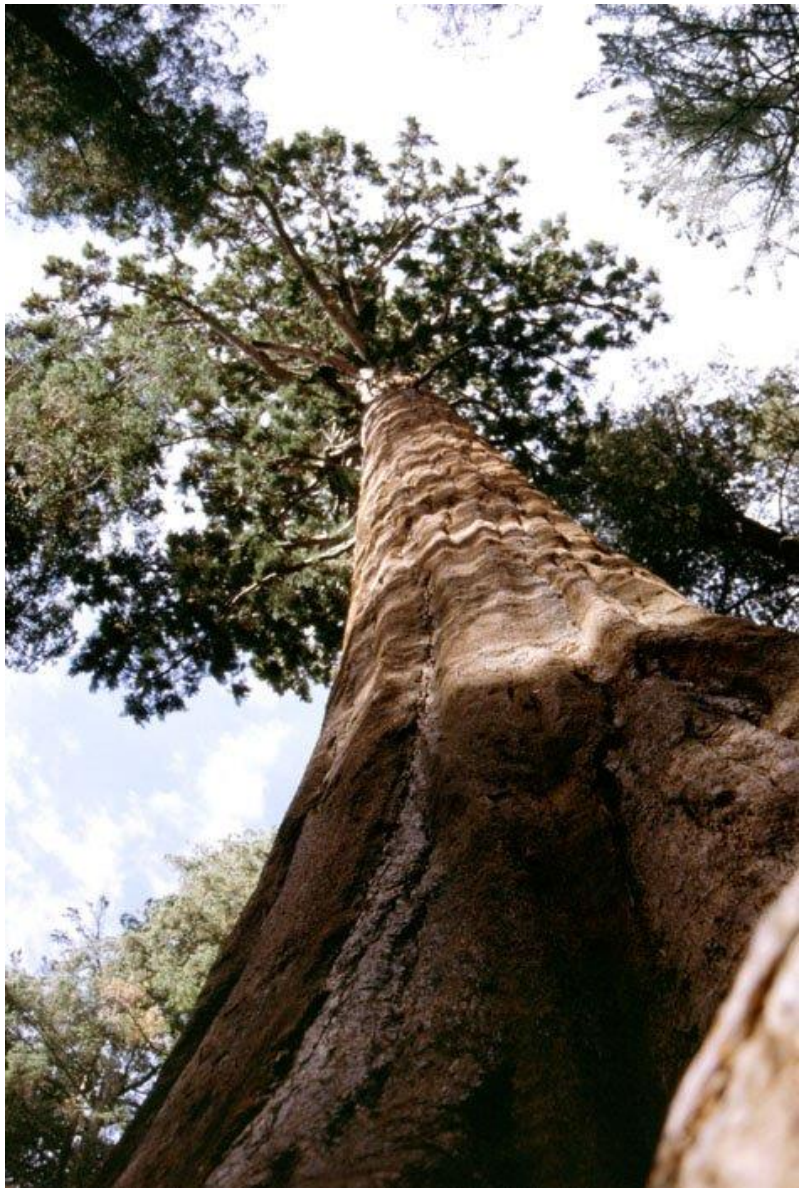
Mechanical properties are highly dependent on strain rate (viscoelastic material, on hydration (normal working conditions of bone in moist environment), on direction of loading (anisotropic material).

Material properties (hardness, stiffness, toughness) depend on degree of mineralization (very high in whale bulla, enamel; low in antler).

Adaptive growth of bone: material laid down where needed, removed where not needed (balance of bone deposition by osteoblasts and bone resorption by osteoclasts)

Examples of deseased bone: osteoporosis, osteogenesis imperfecta

9. Wood



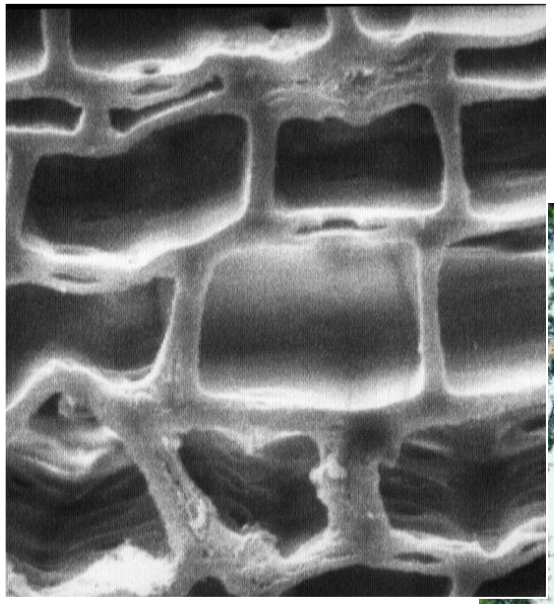
9. Wood

Light weight materials bone and wood

Both are cellular materials used for large structures

Bone

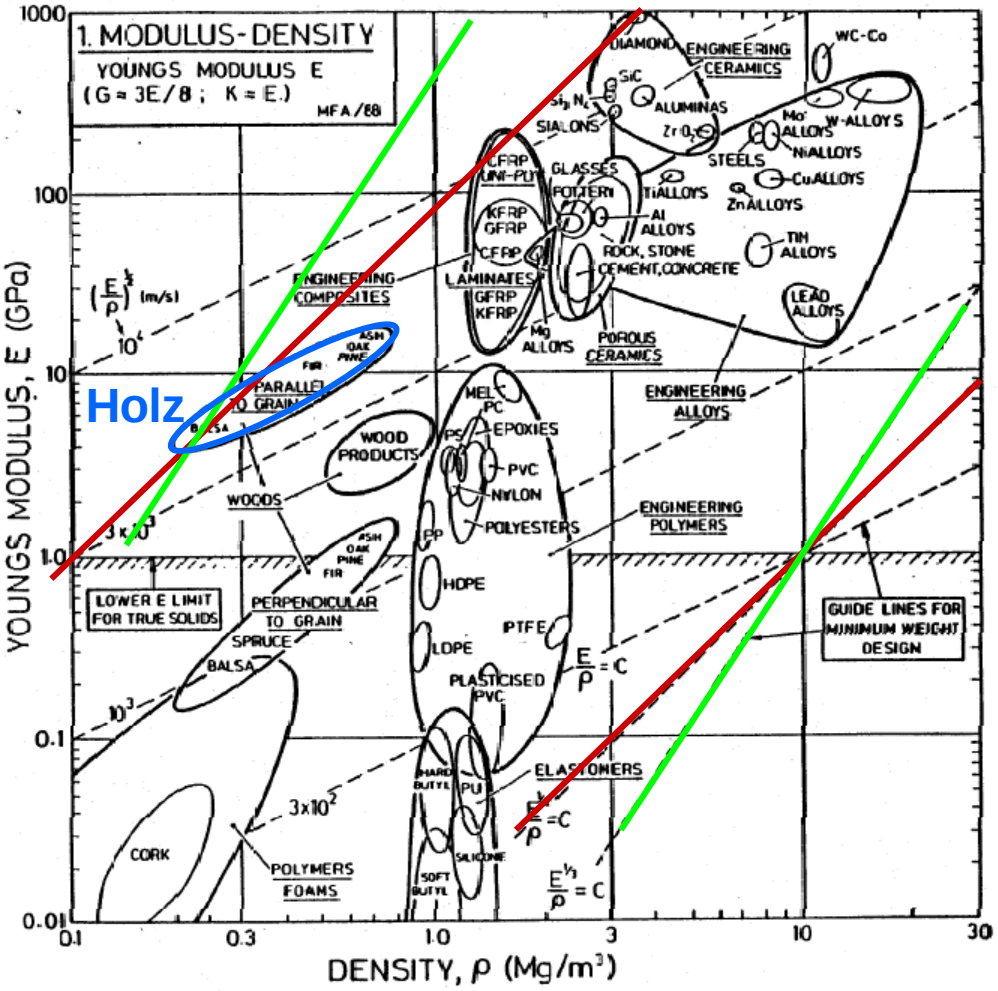
Wood



9. Wood

Mechanical optimization of wood

Remember Ashby plot: wood is an ideal material for column that should not buckle under its own weight (and that of the crown).



$P/W \propto E/\rho^2$

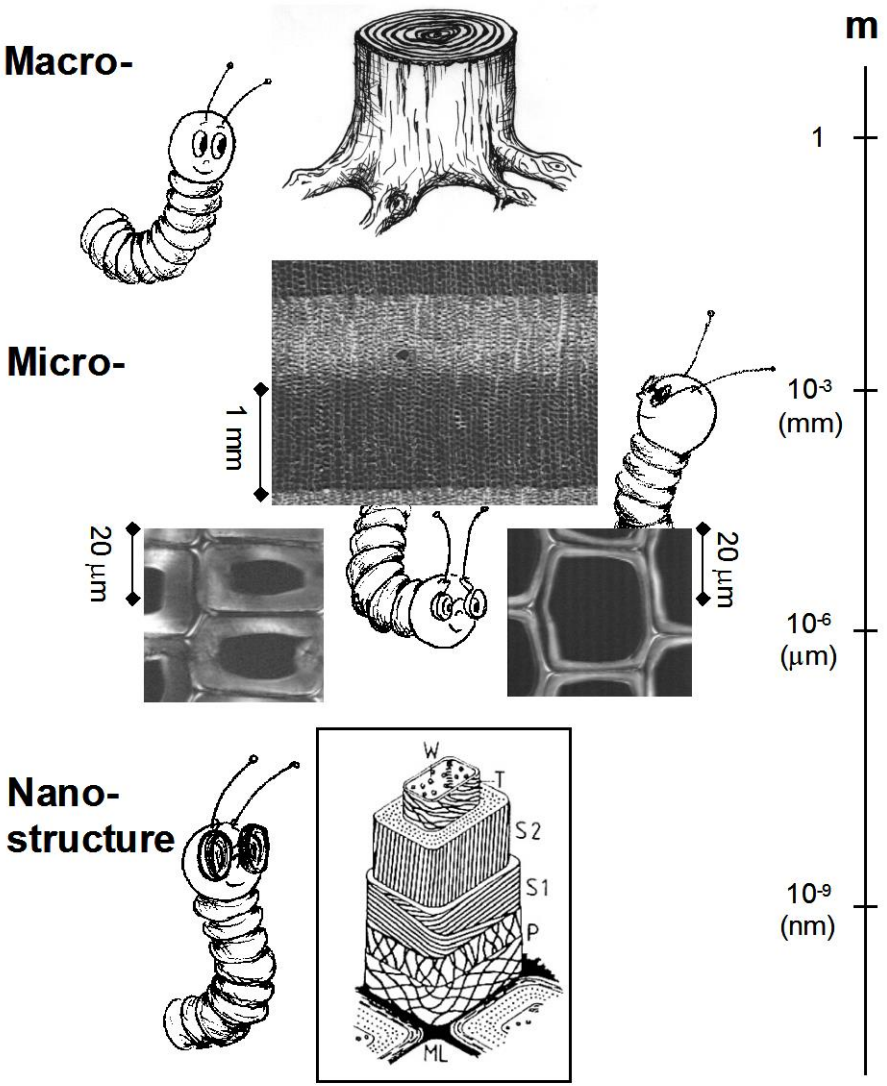
column loaded in compression, resist buckling

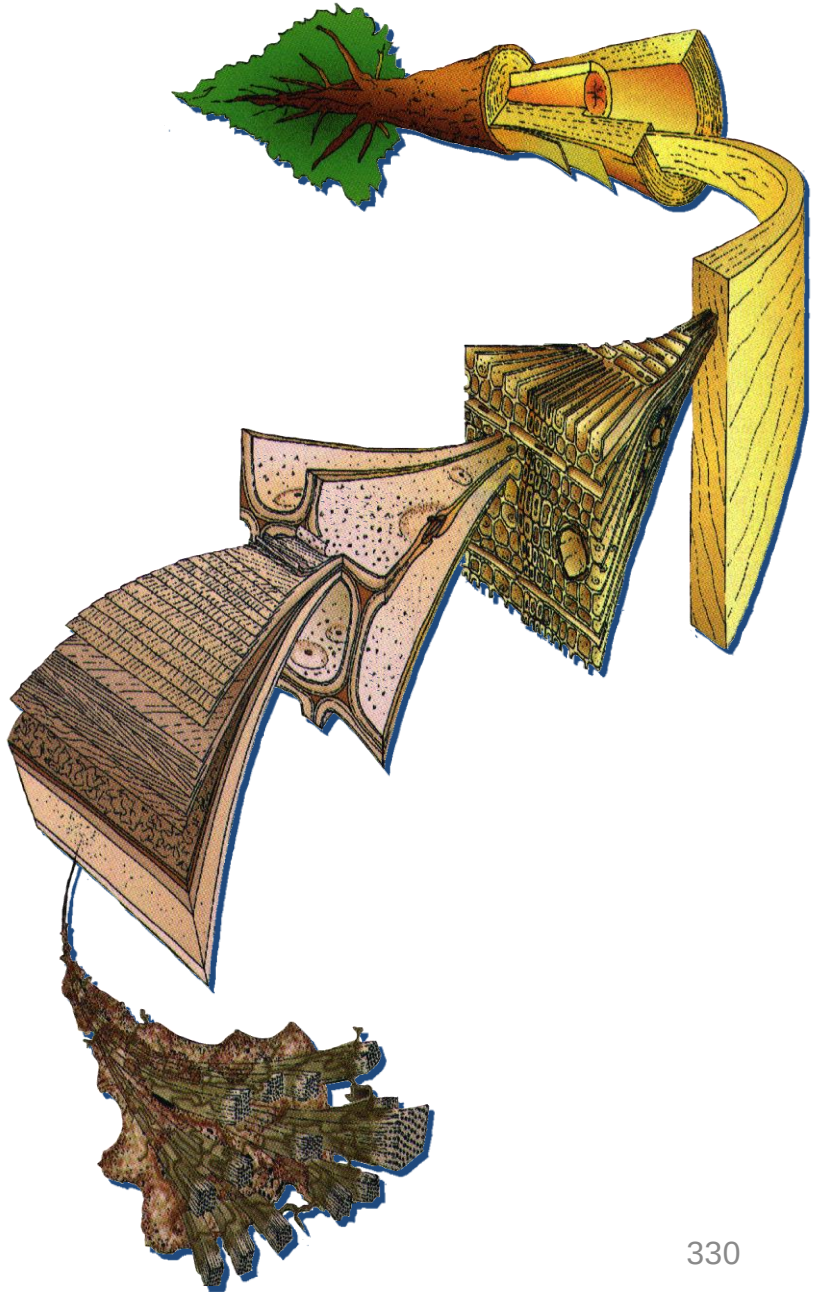
$P/W \propto E/\rho^3$

beam, minimize bending

9. Wood

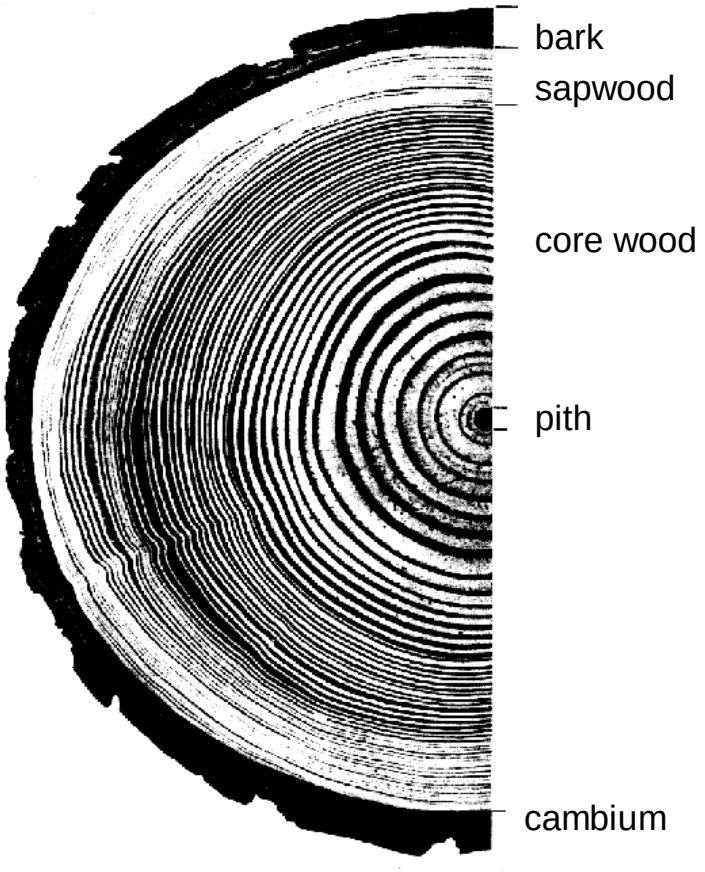
Hierarchical structure of wood





9. Wood

Macroscopic scale: annual rings



bark = dead tissue, protection

sapwood: dead tissue, open cells for transport of water and nutrients

core wood: dead tissue, older, cells closed (protection against rotting)

pith: living cells

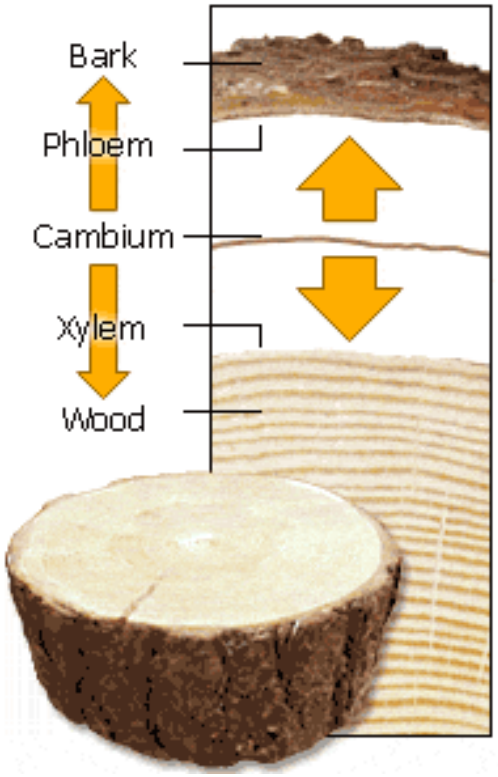
cambium: sheath of living cells (region of growth) between bark and wood

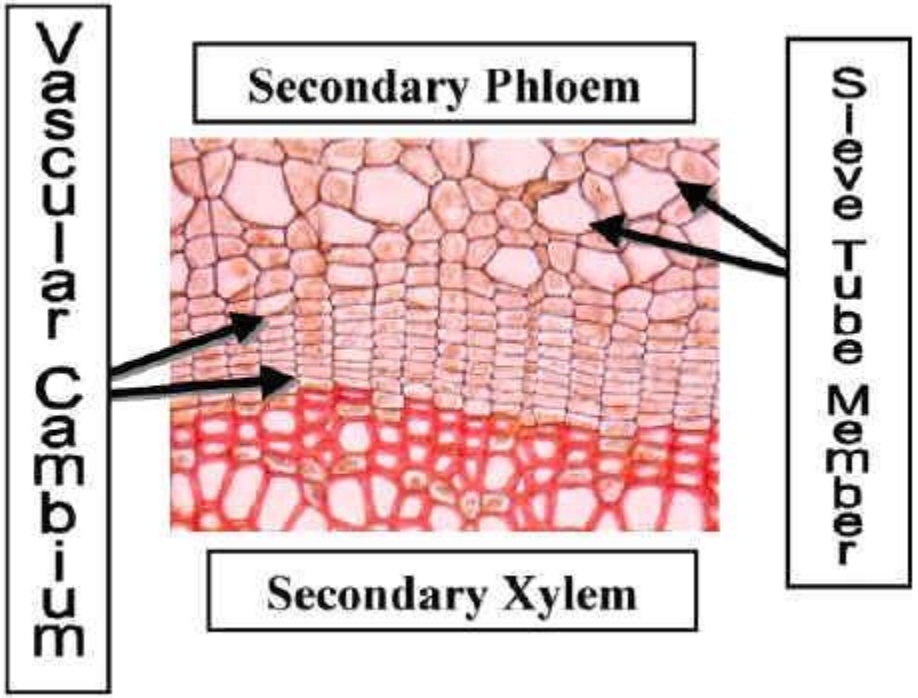
9. Wood

Wood growth

Starts from cambium. Cells develop to either side:

- Bark: towards the outside of the stem
- Wood: towards the inside. Both are dead tissues.



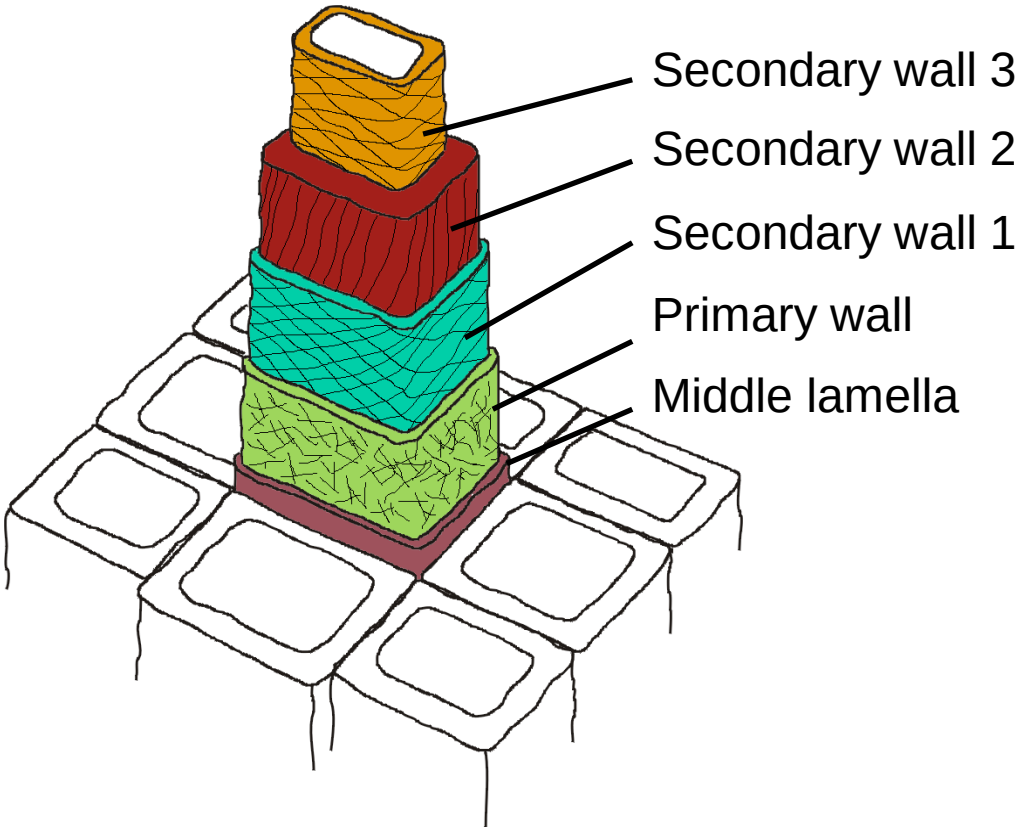


9. Wood

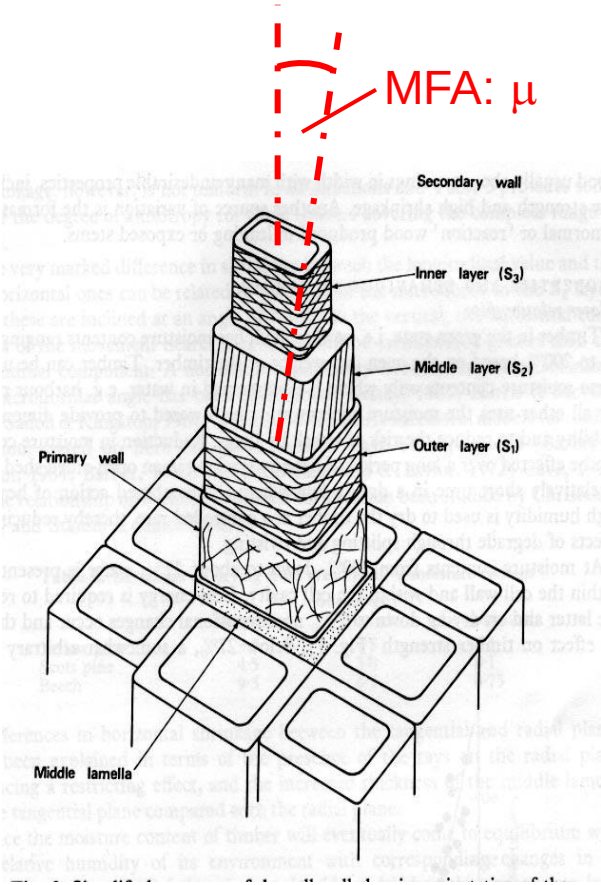
Cell wall structure – microfibril angle

Starts from cambium. Cells develop to either side:

- Bark: towards the outside of the stem
- Wood: towards the inside. Both are dead tissues.



MFA: fibril angle in S2 (thickest layer)



9. Wood

Chemical composition of wood

C 49%, H 6%, O 44%, N trace, inorganic ash Na, K, Ca, Mg, Si

Polymers in wood are

- cellulose 40-44% (hardwoods) 40-44%(softwoods)
- hemicellulose 15-35% (hardwoods) 30-32%(softwoods)
- lignin 18-25% (hardwoods) 25-32% (softwoods)

Cellulose is present in partly crystalline form, matrix amourphous.

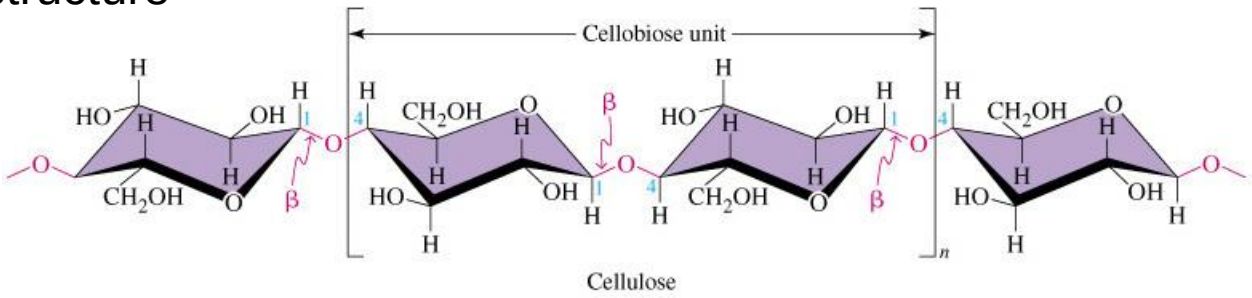
Crystalline and amorphous regions in cellulose:

crystalline regions	amorphous regions
highly ordered parallel arrangements	LOR (less ordered regions)
account for 60-70% (depending on the source of cellulose)	parallel arrangement breaks down
difficult to penetrate with chemicals	more readily penetrated

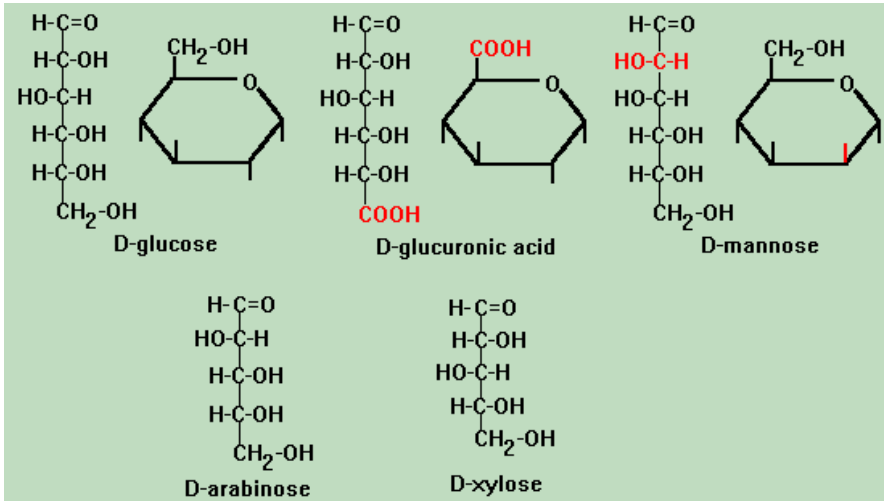
9. Wood

Cellulose

Molecular structure



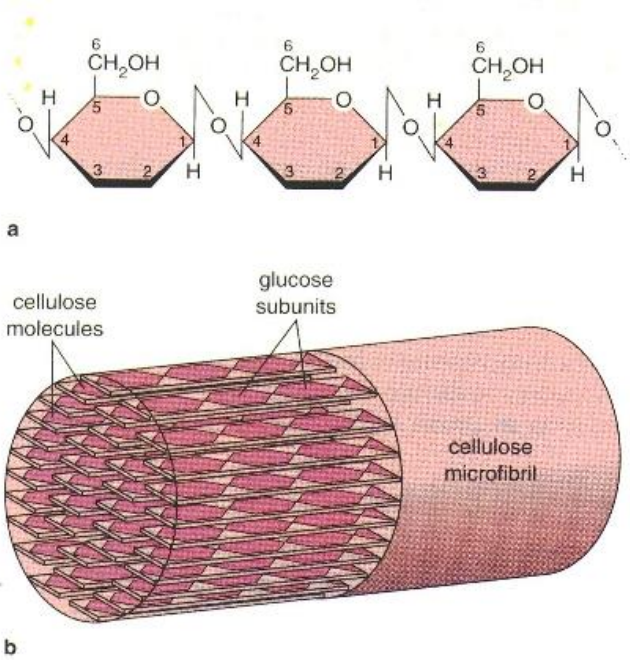
Hemicellulose, structure of monomers

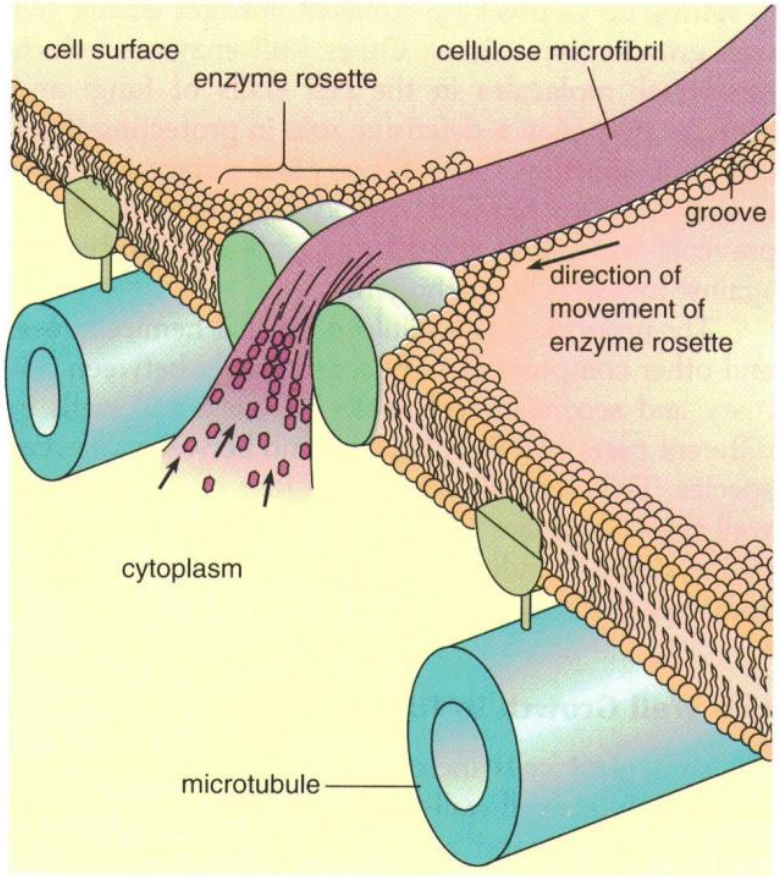


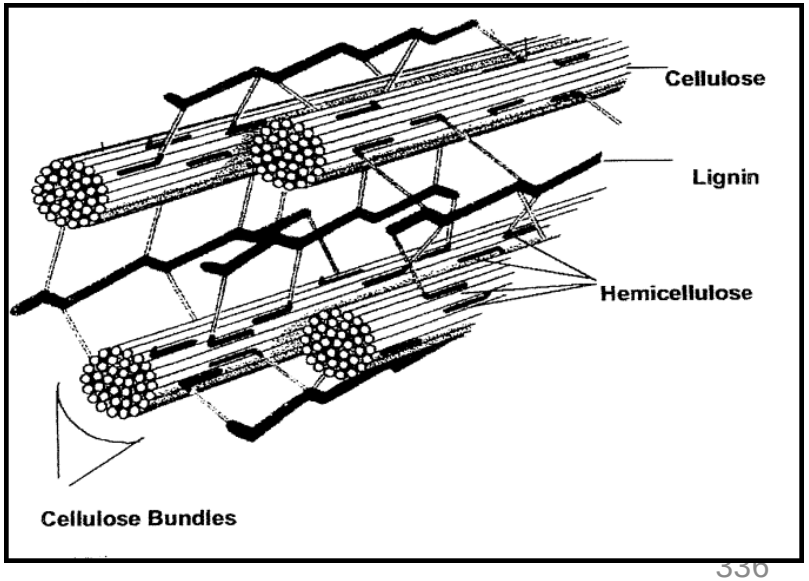
9. Wood

Synthesis of cellulose fibers

By enzyme rosette moving along microtubules and spinning cellulose fibers.



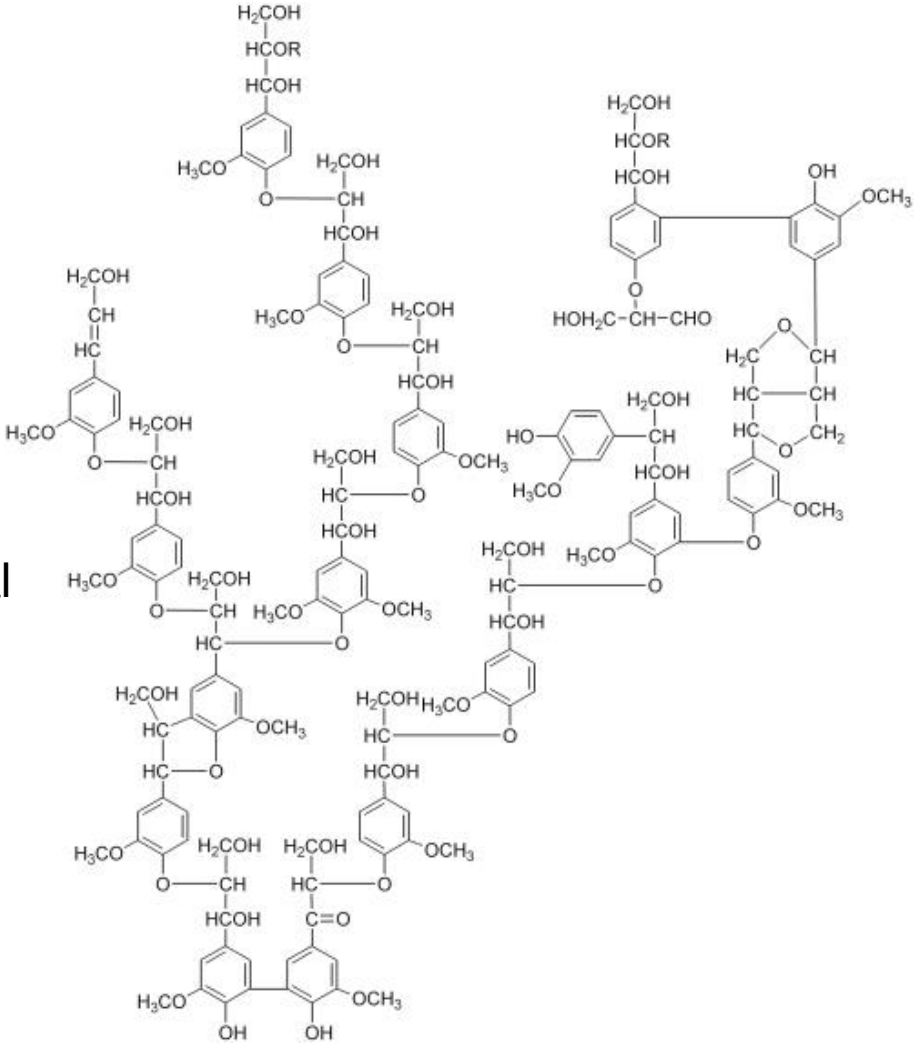


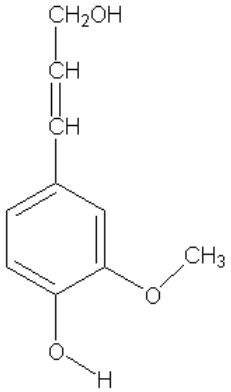


9. Wood

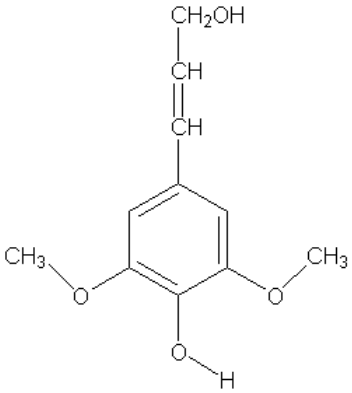
Lignin

- complex aromatic, organic polymer
- no simple repeat unit
- hydrophobic-repels water
- acts as an adhesive in cell wall
- stiffens wood
- removal of lignin is object of chemical pulping and bleaching





Coniferyl alcohol: occurs only in softwoods

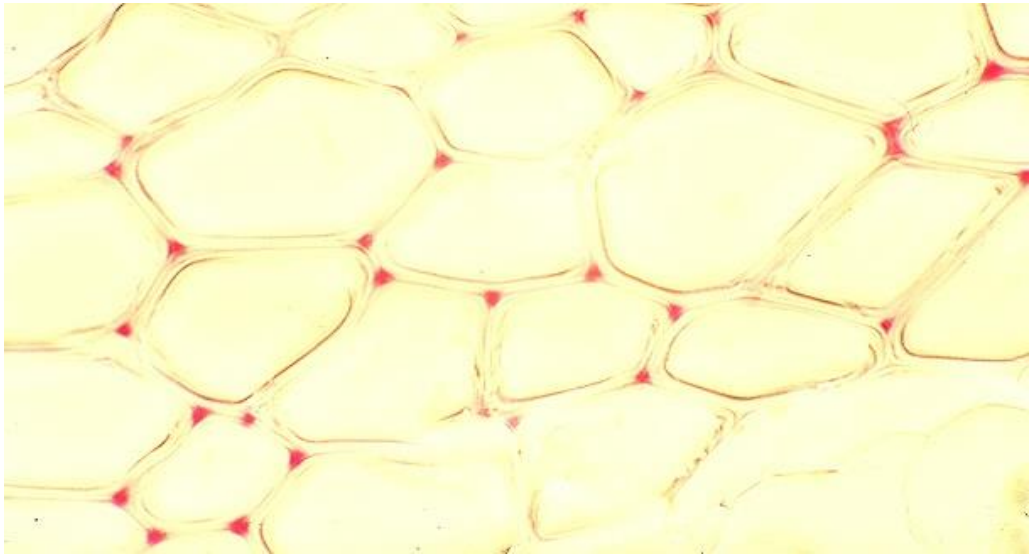


Sinapyl alcohol. Both coniferyl and sinapyl alcohol occur in hardwoods

9. Wood

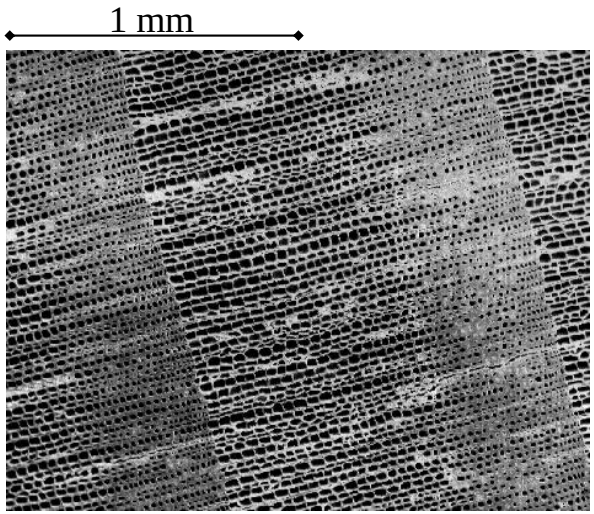
Lignification

Incorporation of lignin into pre-formed wood cell walls consisting of cellulose.



9. Wood

Wood cells in Norway spruce wood



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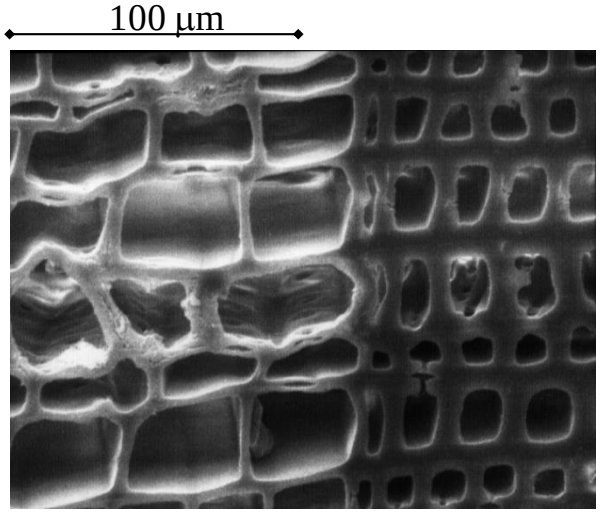

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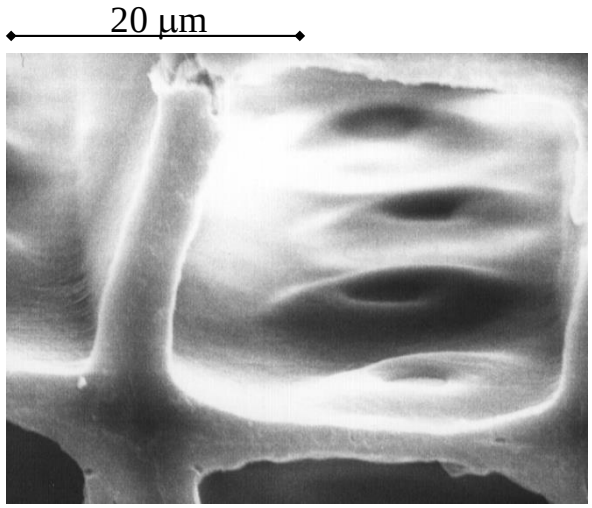

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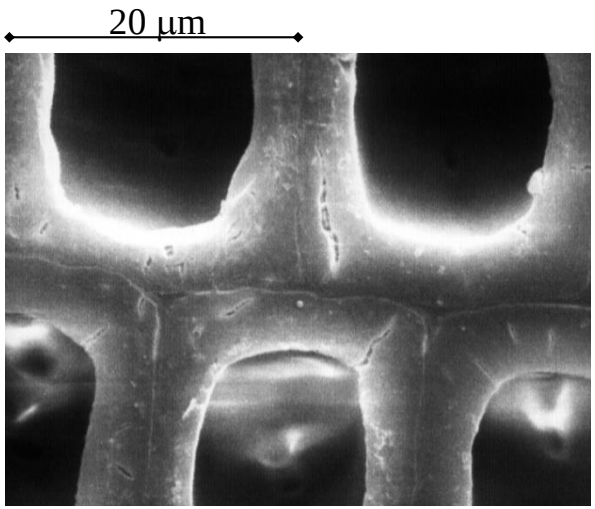
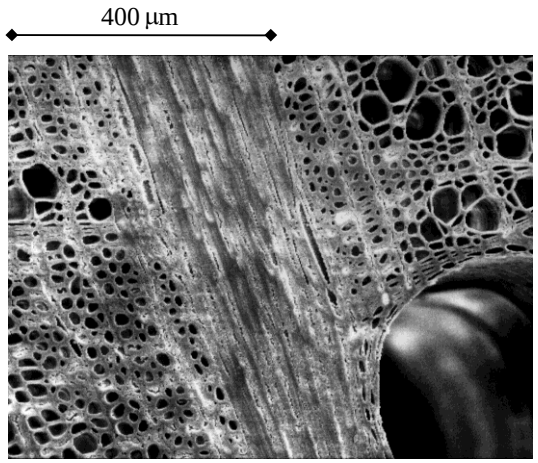


d

9. Wood

Wood cells in Oak



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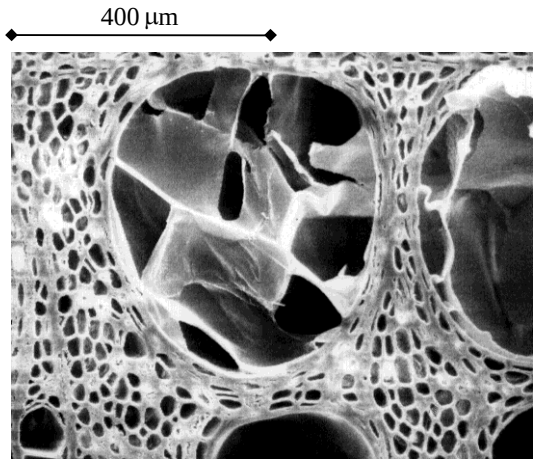

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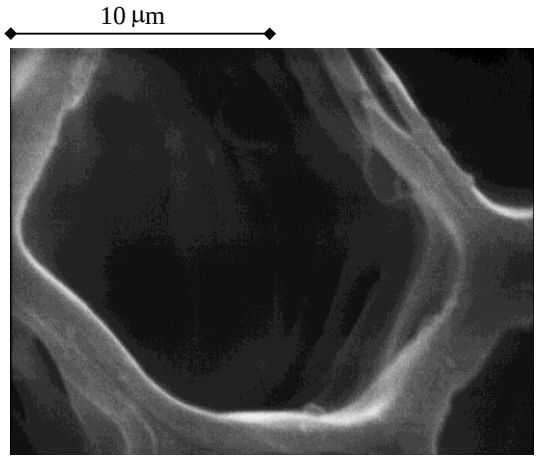

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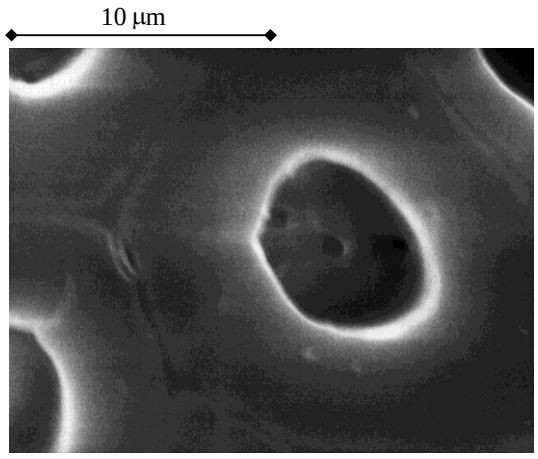

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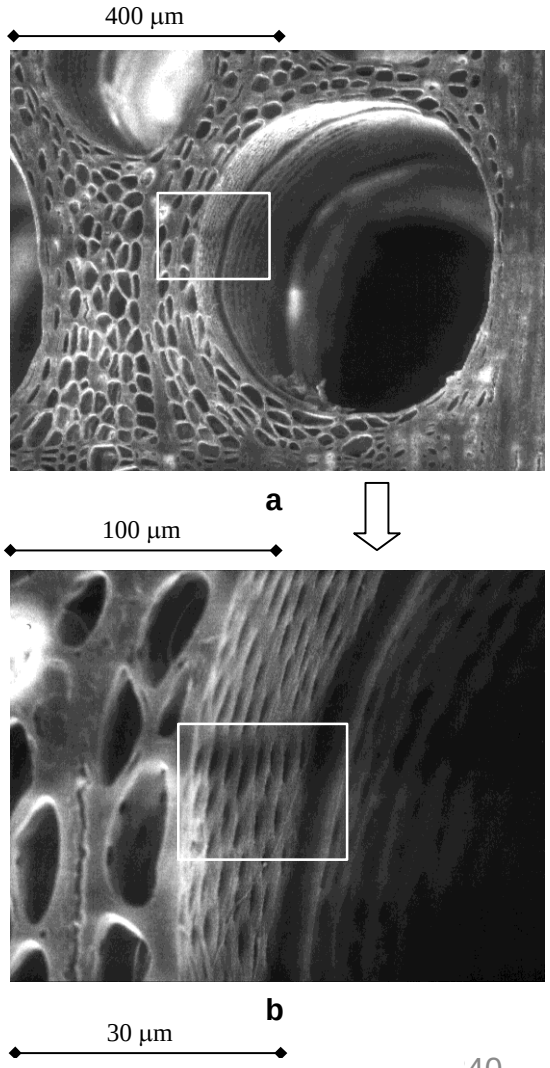
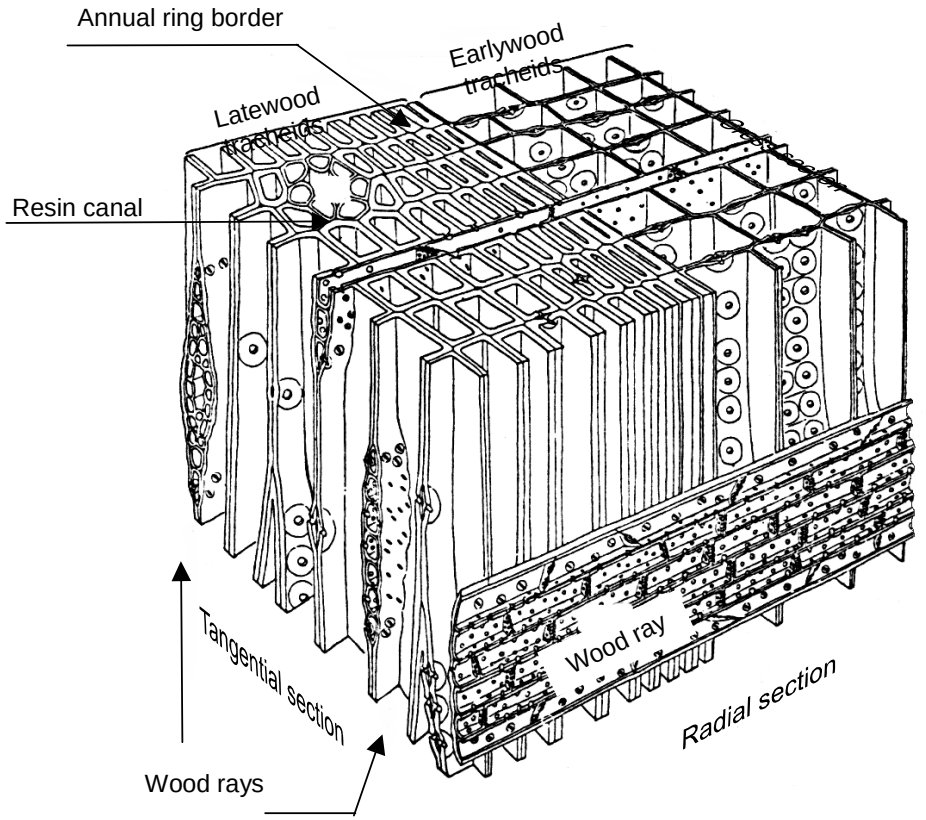


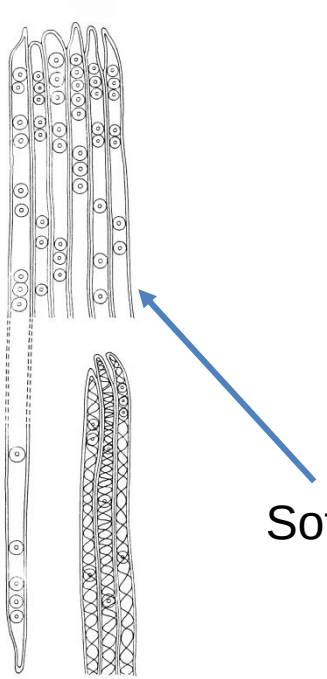
9. Wood

Wood anatomy

Softwood: simpler and evolutionary older.

Multipurpose cells: tracheids, provide water transport and mechanical support.





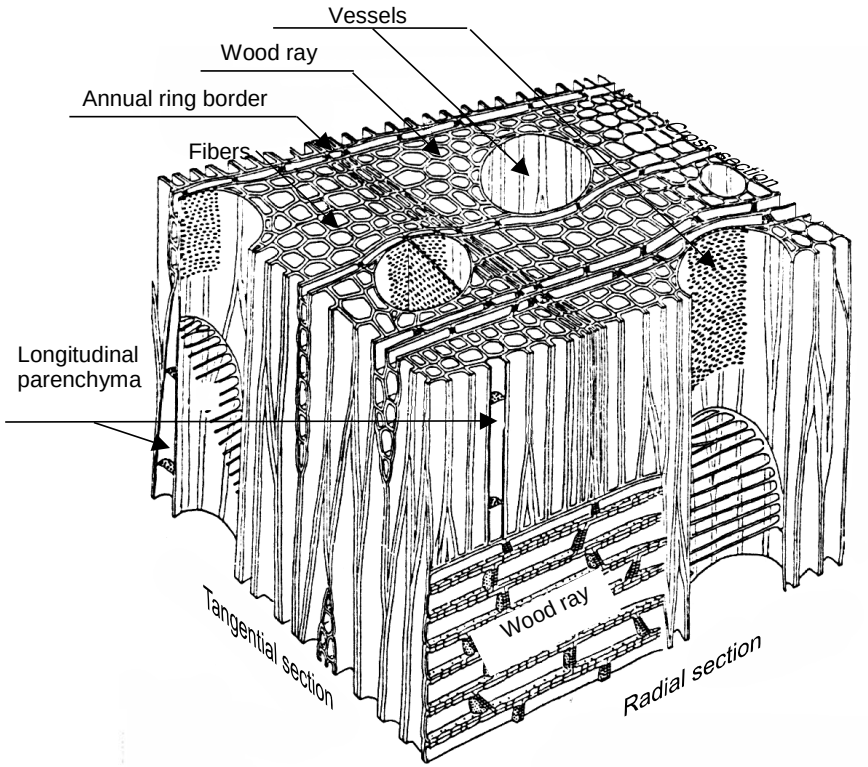
Soft wood tracheid (length 2 to 6 mm)

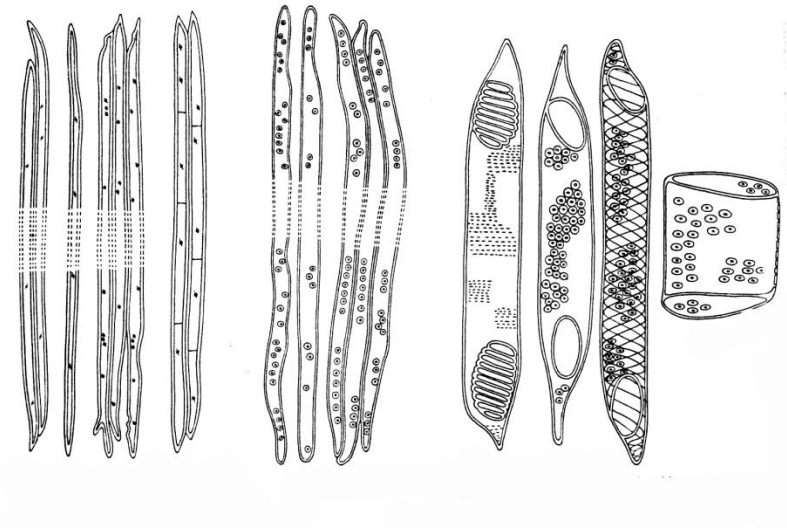
9. Wood

Wood anatomy

Hardwood: more complex, evolutionary younger.

Specialized cells for different purposes: ligniform fibers for support, vessels for water transport.



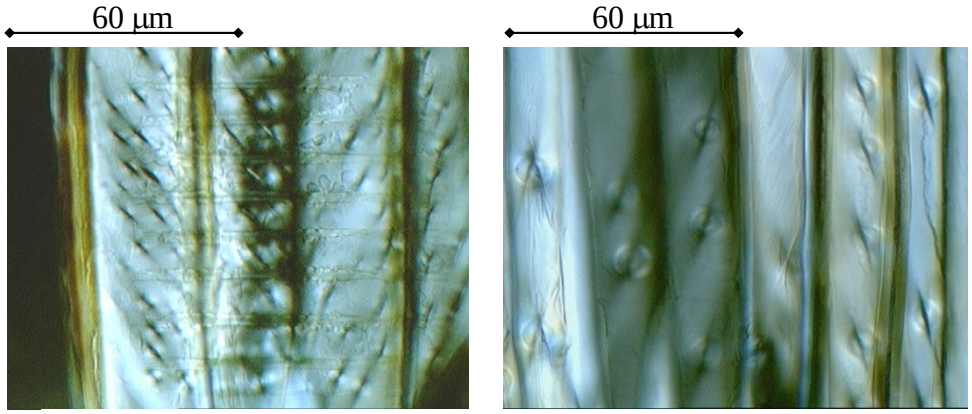


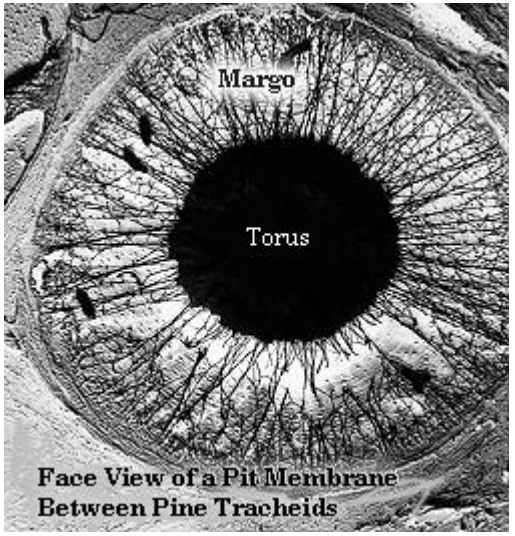
Hardwood vessels (fluid conducted over a distance from 10 cm to 10 m by addition sequential addition of vessels)

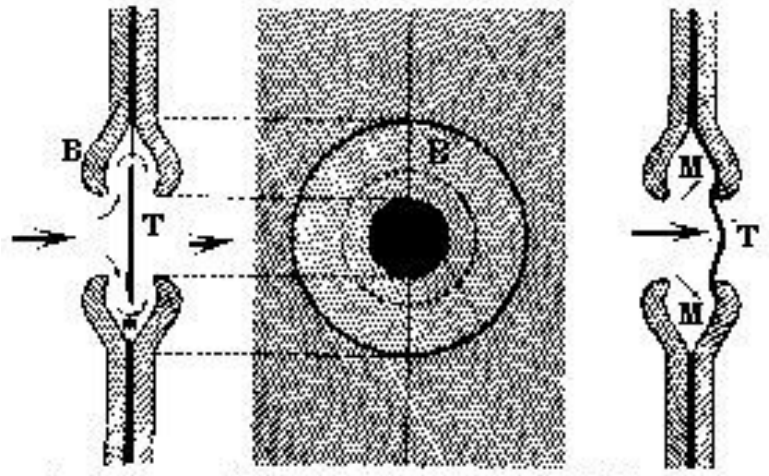
9. Wood

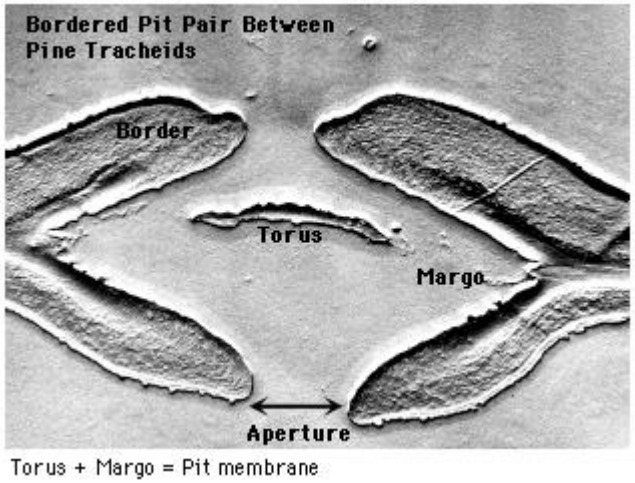
Pits

Connection between adjacent tracheids







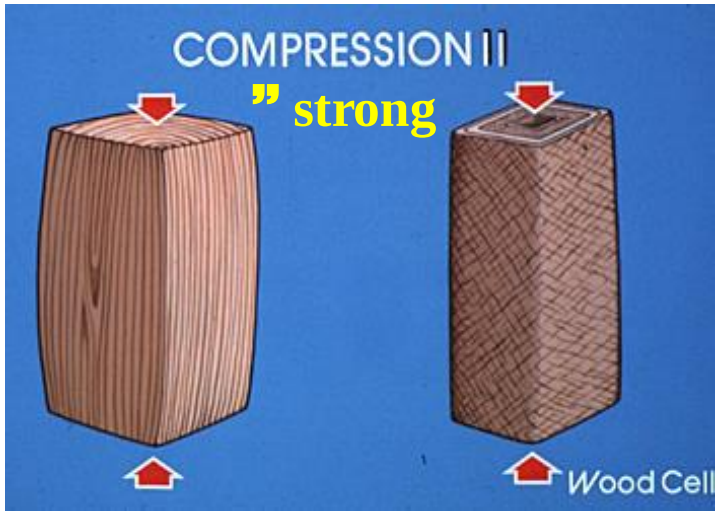


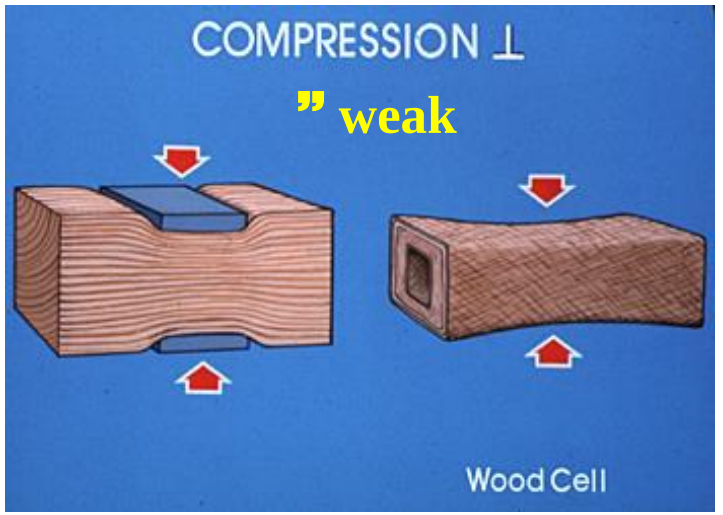
Torus + Margo = Pit membrane

Bordered pits work like valves to avoid loss of fluid and pressure

9. Wood

Mechanical anisotropy of wood



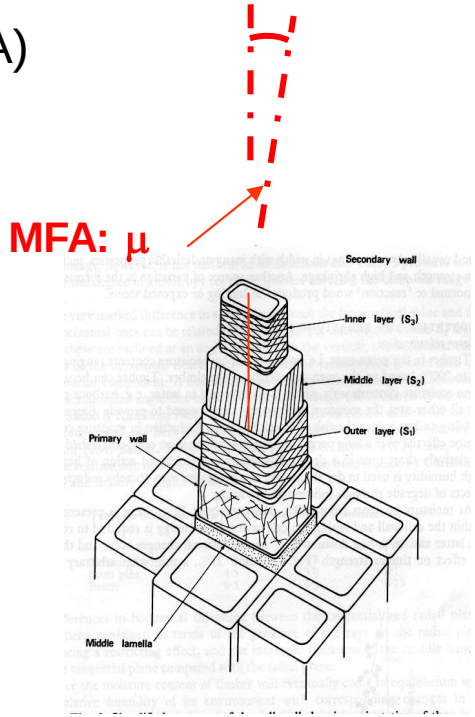


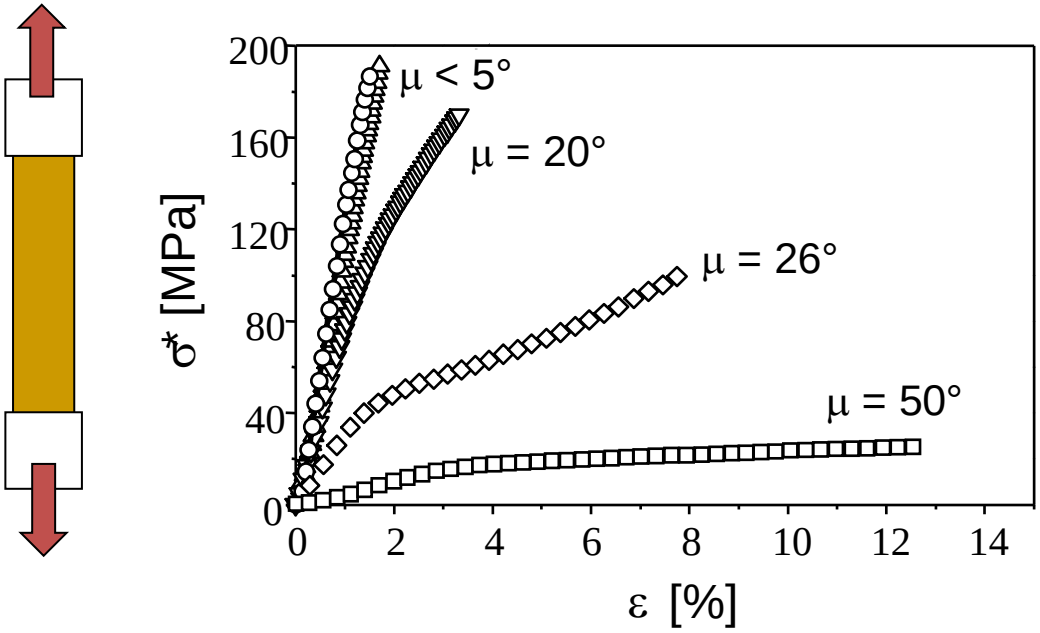
9. Wood

Ultrastructure and mechanical properties

Behavior of spruce wood with different microfibril angle (MFA) in tension:

Higher MFA leads to softer, but more extensible material.



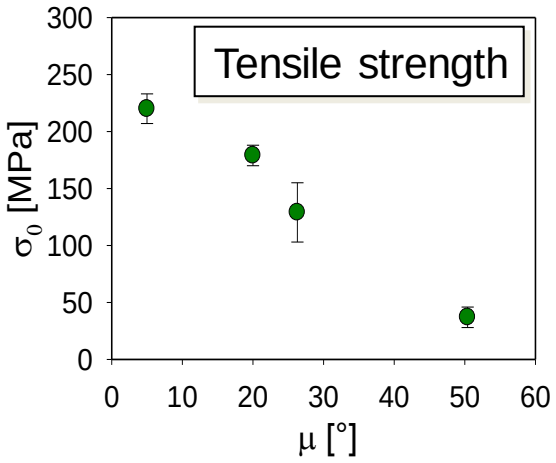


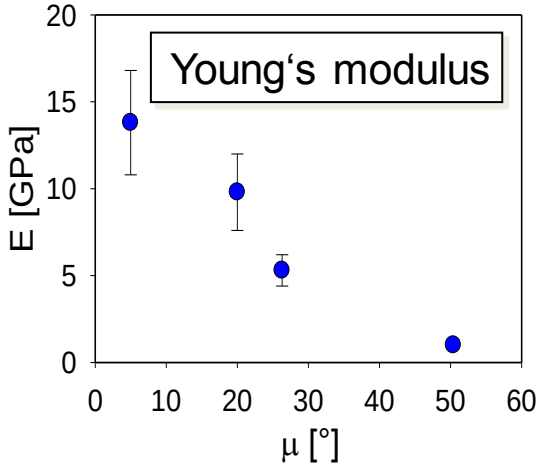
9. Wood

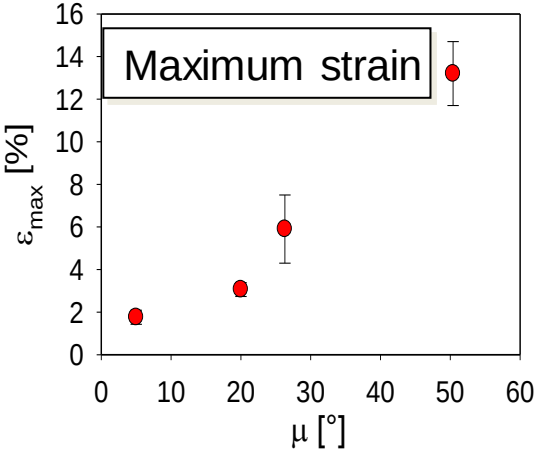
Ultrastructure and mechanical properties

Behavior of spruce wood with different microfibril angle (MFA) in tension:

- Tensile strength decreases with increasing MFA
- Stiffness (Young‘s modulus) decreases with increasing MFA
- Maximum strain increases with increasing MFA

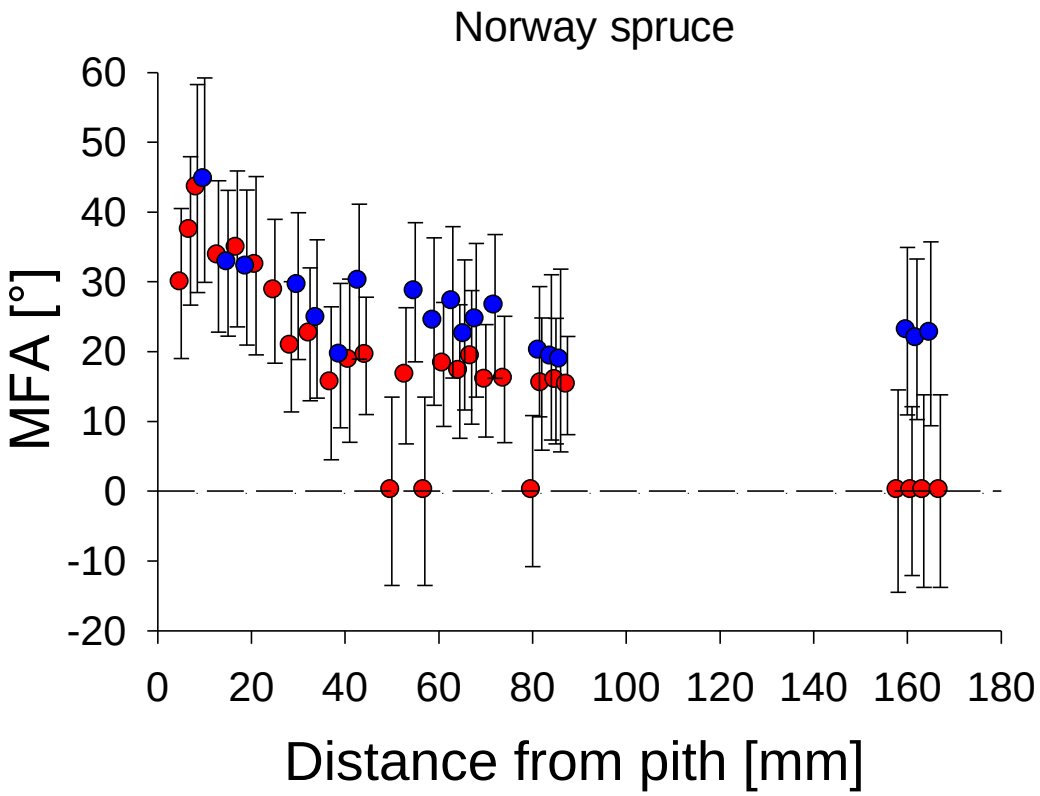






9. Wood

Variation of MFA within single stem

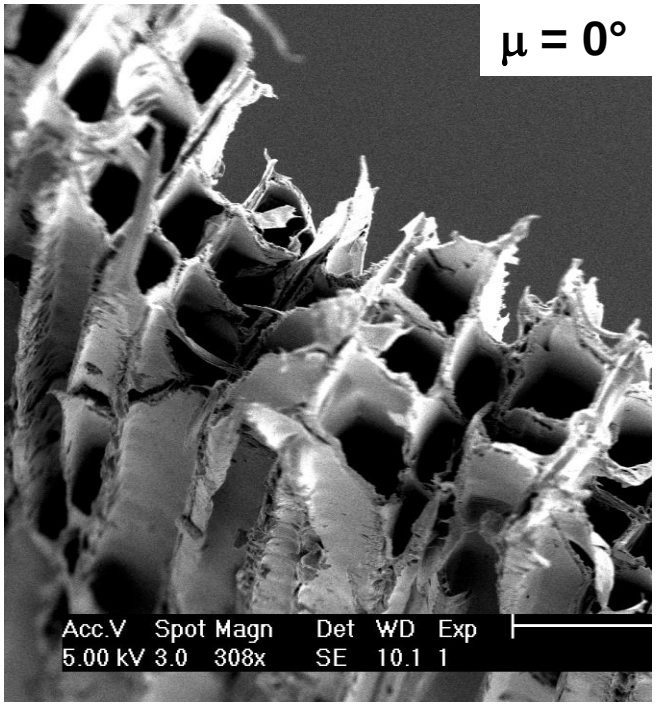


9. Wood

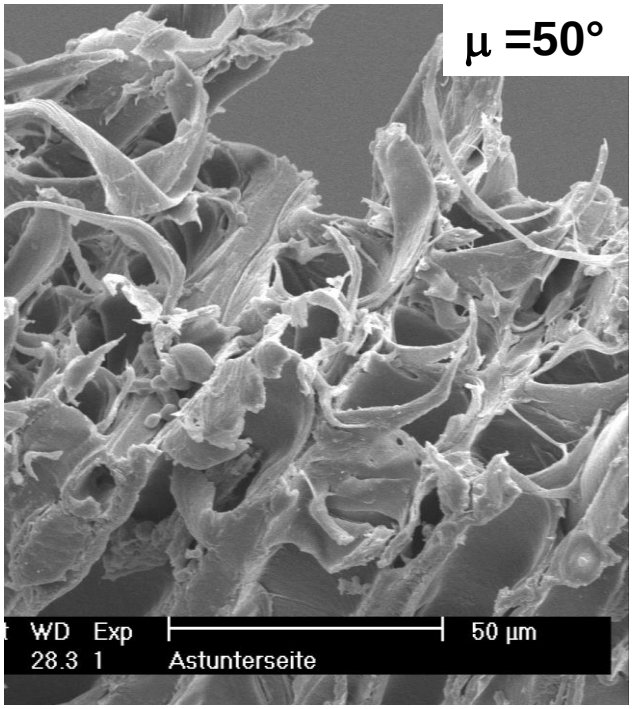
Fracture of wood with different MFA

Wood with small MFA fractures in a brittle way.

Wood with large MFA is heavily deformed (spiral pull out) before breaking.



brittle fracture



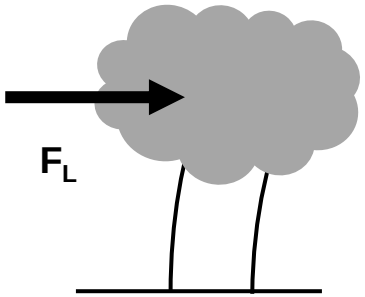
plastic deformation

9. Wood

Mechanical optimization of trees

Cylindrical stem:

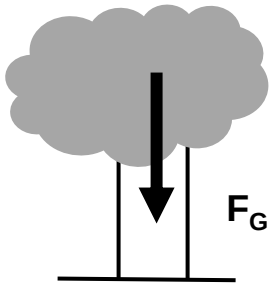
Lateral forces



$$\sigma_0 > \frac{D\,H\,F_L}{2I}$$

Optimization on **strength**

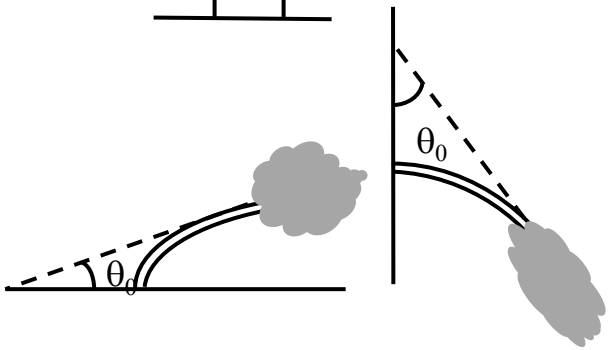
Compressive force (weight)



$$E > \frac{4\,H^2\,F_G}{I\,\pi^2}$$

Optimization on **stiffness**

Bending to a critical angle

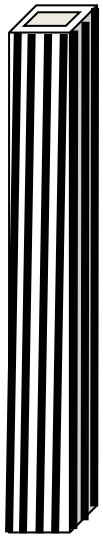


$$\varepsilon_0 > \frac{D}{H} \cdot \frac{\lambda_0}{2}$$

Optimization on **extensibility**

9. Wood

Rigidity versus flexibility

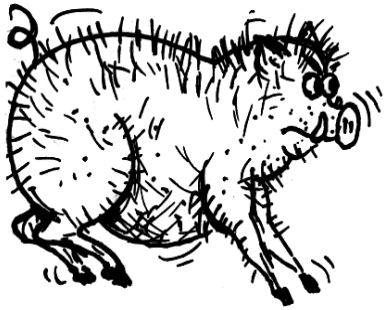


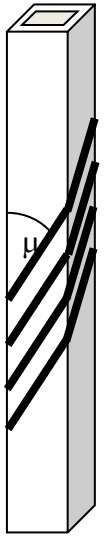
Older trees

Rigidity
Stiffness

Young trees, branches

Flexibility
Toughness





H. Lichtenegger, A. Reiterer, S.E. Stanzl-Tschegg, and P. Fratzl.. *Journal of Structural Biology* 128 (3), 257-269 (1999).

9. Wood

Summary Wood

Wood is **light weight material** optimized to support its own weight without buckling.

Hierarchical architecture: tree rings, cellular structure, nanocomposite of cellulose fibers (stiff, partially crystalline) and matrix (amorphous, hemicellulose/lignin).

Growth of tree: by adding material only! (no change of existing material).
Growth zone: cambium (between wood and bark)

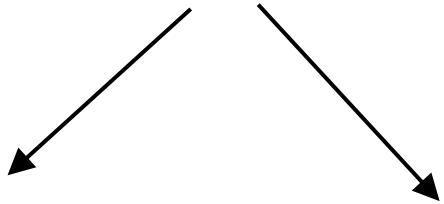
Wood cells arrange to build up complex vessel system: bordered pits act as valves between cells.

Ultrastructure and mechanical properties:
Microfibril angle (MFA) influences stiffness, extensibility and toughness of wood.
Optimization of different parts of tree:
branches, wood near pith: large MFA (toughness, flexibility)
large stems: small MFA (stiffness)

10. Smart materials – adaptive growth

Smart materials - no-maintenance materials

- reasonable start design
- self regulation
- self-repairing (wound healing)
- adaptation to changing environment



Adaptation strategies in bone

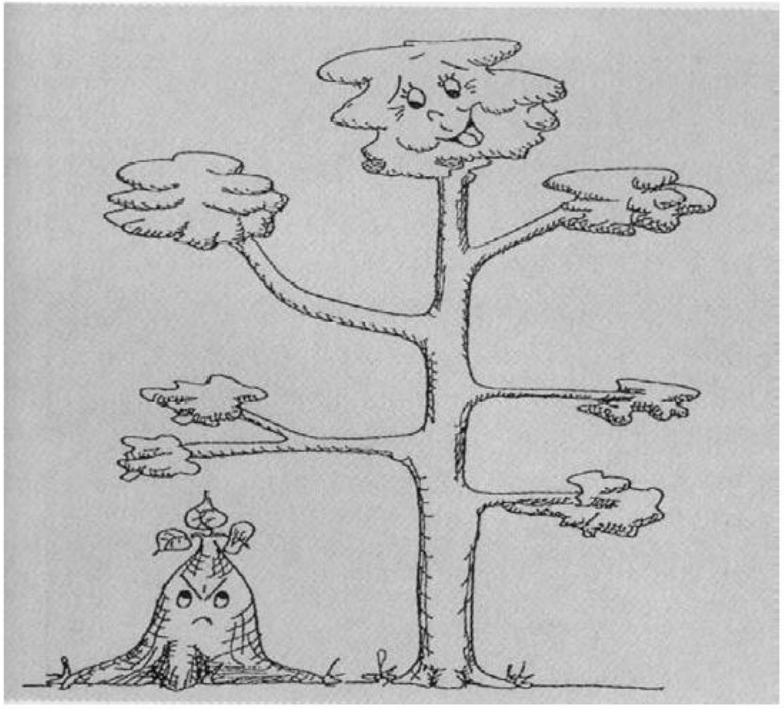
Adaptation strategies in wood

10. Smart materials – adaptive growth

10.1 Reasonable start design – safety factor

Safety factor: ratio of strength (structural capacity) to actual applied (or normally expected) load.

How much safety does a living organism need?



Material	Safety factor
Bones	2-6
Tree trunks	4
Stems of annual plants	2
Buoyancy chambers of mollusks	1.4

Compare with safety factors in technical engineering!

10. Smart materials – adaptive growth

10.2 Adaptation strategies in bone

Bone is a constantly remodeling material.

Complete turnover every few years.

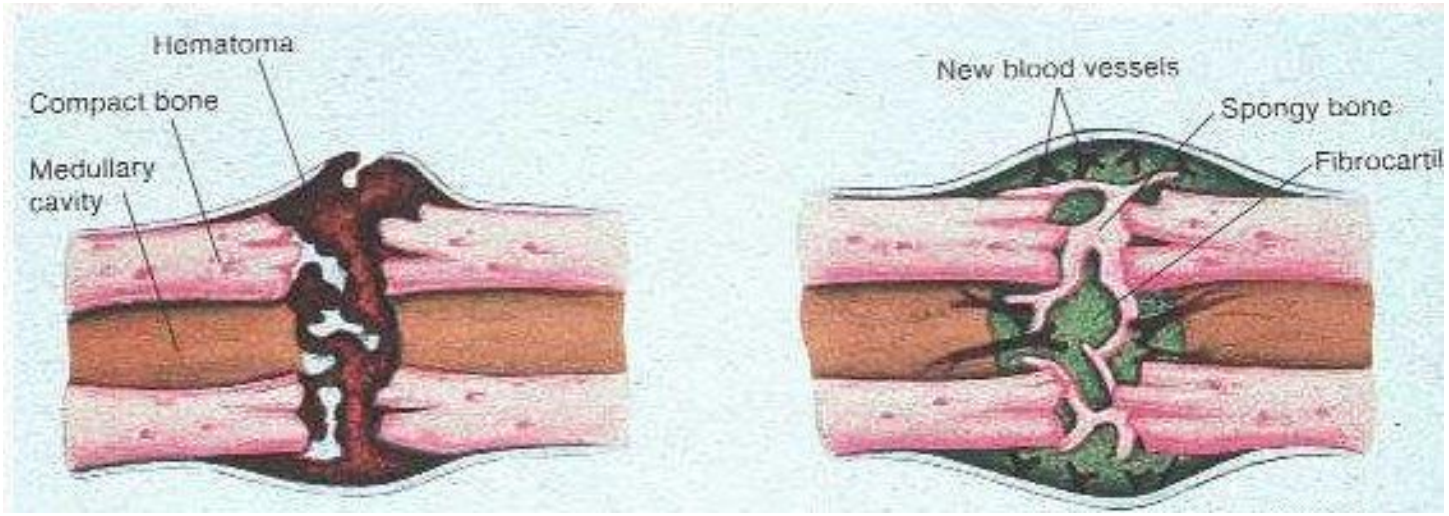
Remodeling by bone cells:

- Osteoblasts (lay down collagen that is later on mineralized)
- Osteoclasts (resorb bone)
- Osteocystes (most likely act as strain sensors)

10. Smart materials – adaptive growth

Self-repair in bone – wound healing

Bone healing after a fracture proceeds in several stages:



1. Inflammation stage:

Blood escapes from ruptured blood vessels and forms a hematoma, patient suffers pain and swelling.

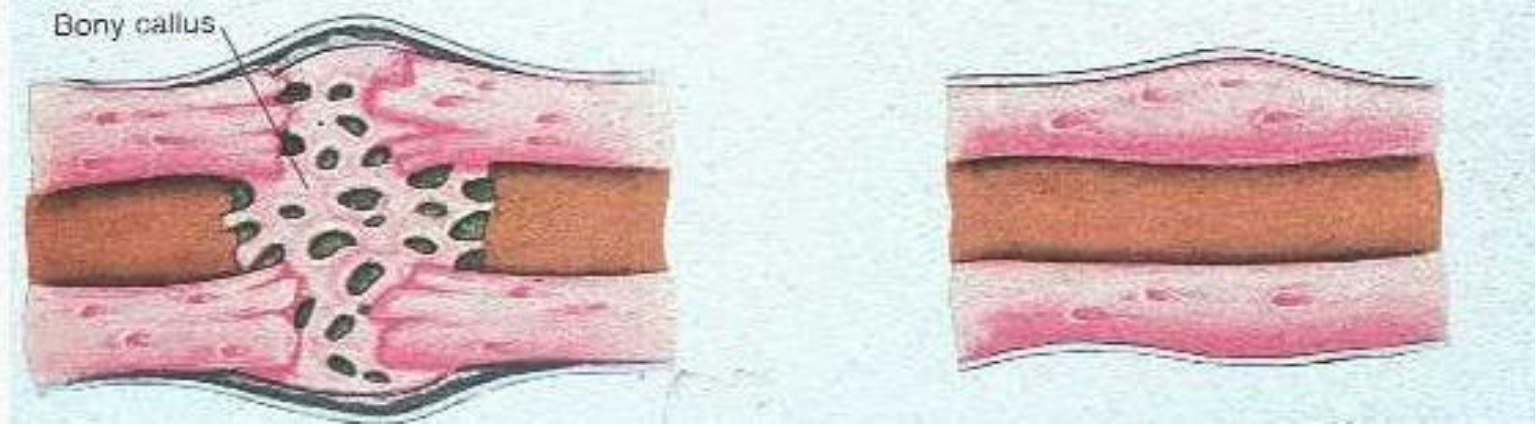
2. Primary soft callus formation:

New blood vessels develop. Spongy bone and fibrocartilage is formed.

Lasts for about 2 weeks.

10. Smart materials – adaptive growth

Self-repair in bone – wound healing



3. Callus mineralization stage:

Fibrocartilage is replaced by a bony callus.

Takes about 4 to 16 weeks and is faster in children and in spongy bone (Crenshaw 1992).

4. Callus remodelling stage

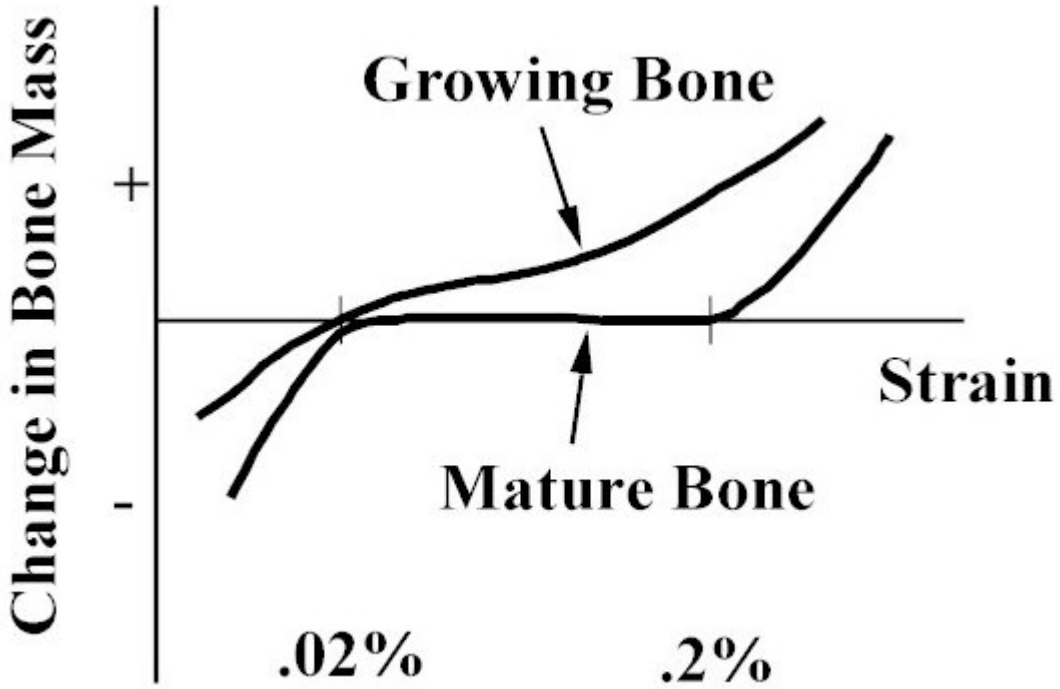
Callus is slowly removed by osteoclasts and replaced with packets of new lamellar bone.

Complete replacement takes 1 to 4 years (Frost 1989).

10. Smart materials – adaptive growth

Optimization of bone mass

Adaptation of bone mass to applied loads:



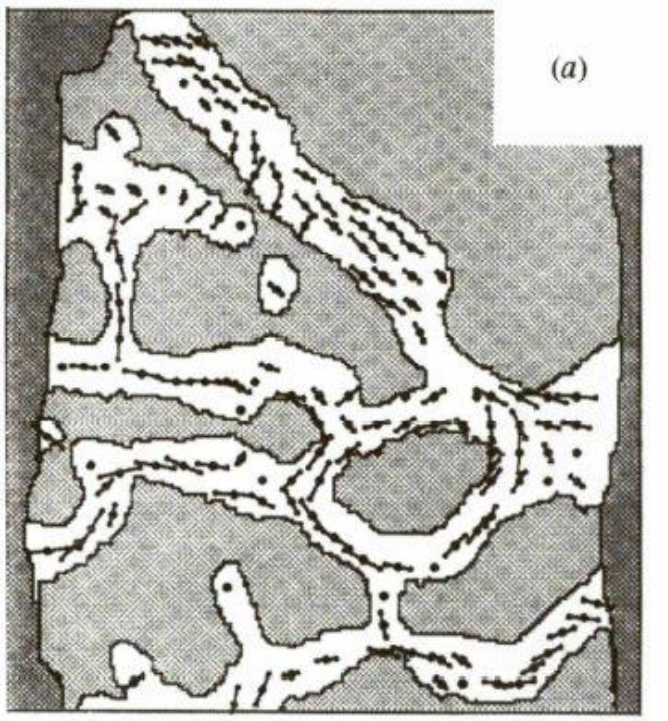
Growing bone reacts to every change in strain.

Mature bone keeps bone mass constant over a range of „normal“ strains, changes only if strain is above or below

10. Smart materials – adaptive growth

Optimization of bone nanostructure

Trabeculae in spongy bone: collagen fibers and HAP crystals are oriented along the longitudinal (loading) direction of the trabecular struts.

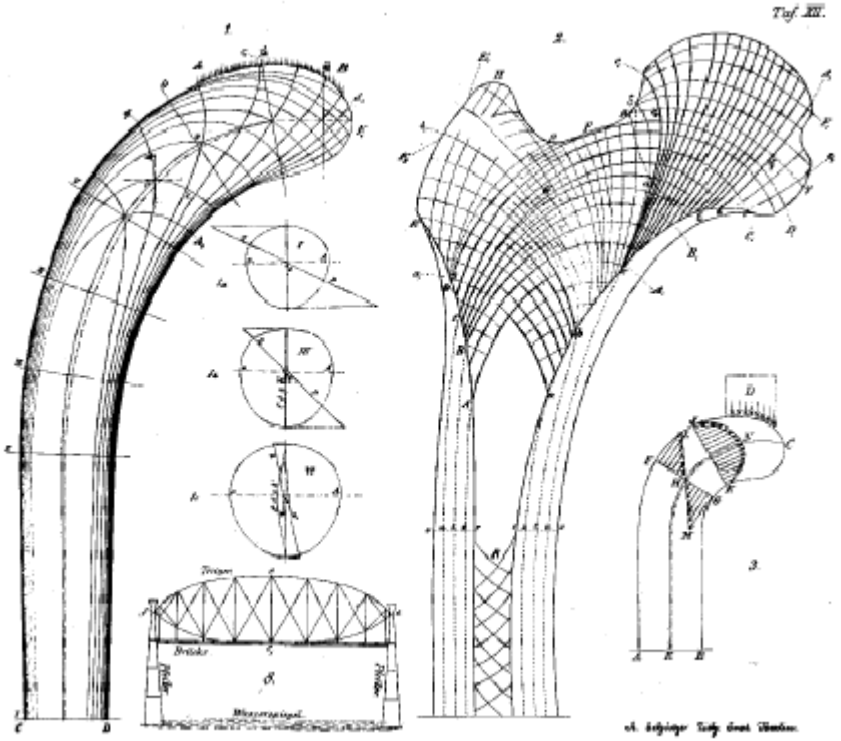


Orientation of mineral particles

10. Smart materials – adaptive growth

Optimization of microstructure

Bone morphology (e.g. trabeculae in spongy bone) adapts according to mechanical requirements.

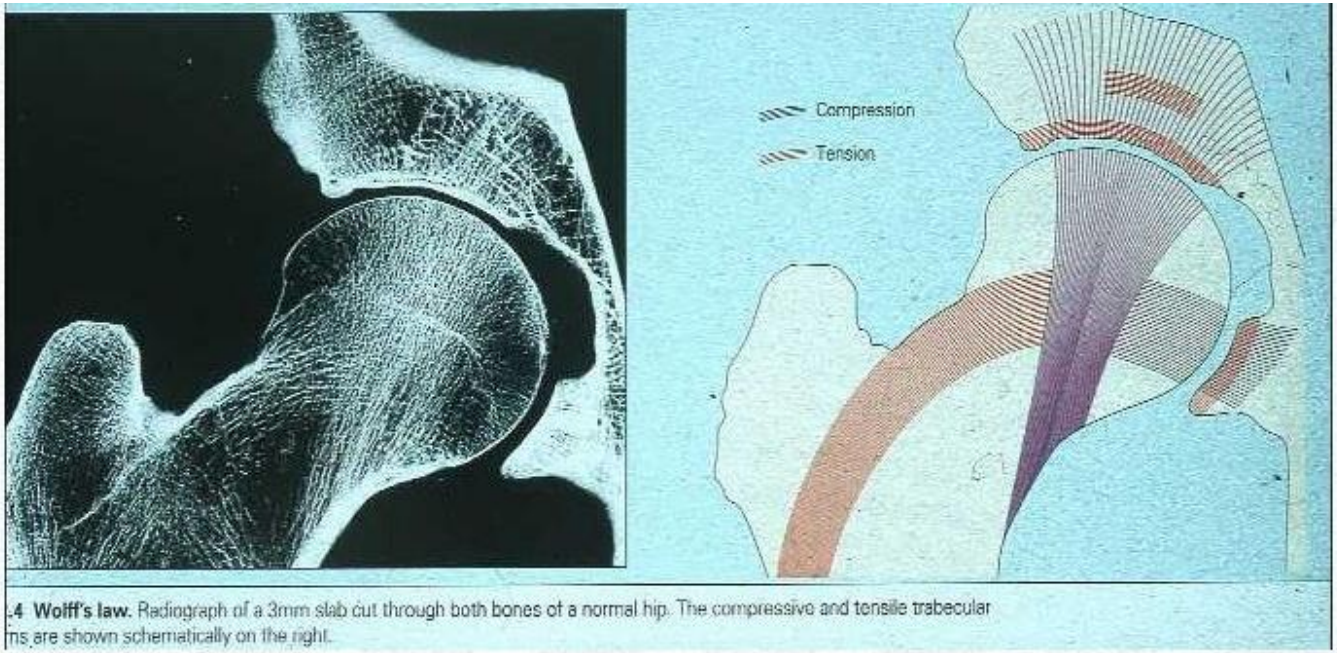


Wolff (1869): Wolff's Law:
"bone adapts (remodels) in response to the mechanical loads placed on it."

10. Smart materials – adaptive growth

Adaptation of spongy bone to stresses

Trabeculae in femur and hip bone follow direction of principal stress (compressive or tensile, depending on part of the hip bone)



.4 **Wolff's law.** Radiograph of a 3mm slab cut through both bones of a normal hip. The compressive and tensile trabecular ns are shown schematically on the right.

Figure 10 - Compression and tension forces on normal hip bone.

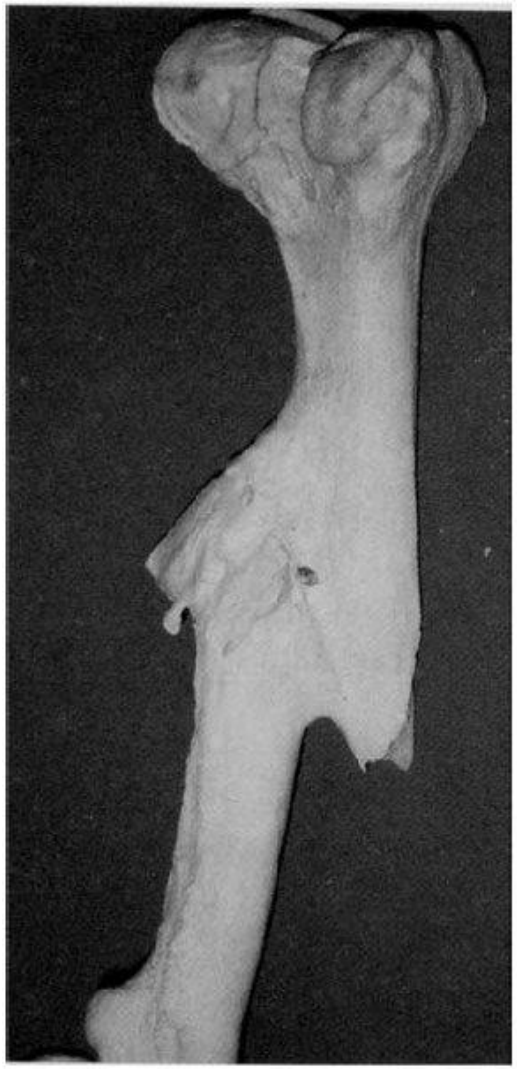
X-ray radiography of hip bone (left) and sketch of compressive and tensile forces (right)

10. Smart materials – adaptive growth

Adaptation exterior bone shape

Bone shape can change dramatically, e.g. after imperfectly aligned fracture.

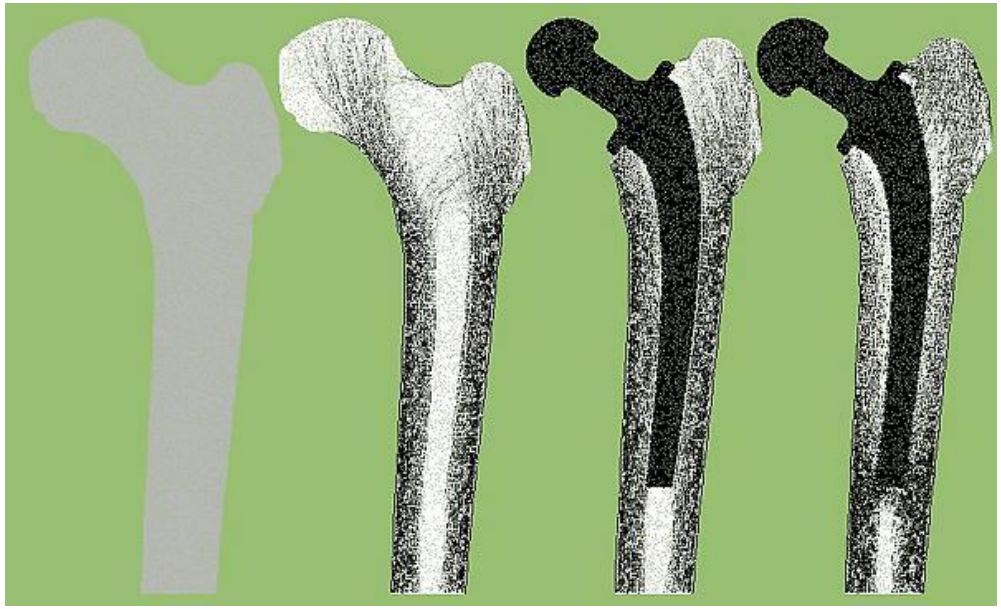
Reduces local stress and improves stability.



10. Smart materials – adaptive growth

The downside of adaptation in bone

E.g. Femur implant: completely changes load distribution in bone.



Denser bone: black, hollow space: white;

Consequences:

bone is laid down at lower end of implant

stress is greatly reduced at the sides of the shaft: bone tissue is removed: implant becomes lose after a certain period of time (about 20-30 years)

10. Smart materials – adaptive growth

Osteoporosis as consequence of adaptation

Microgravity environment causes loss of bone mass due to disuse atrophy, a condition similar to osteoporosis.

Bone loss rate: about 0.2-5% per month, can be lowered to about 0.2 % per month by exercise.

Nevertheless still poses a natural limit to the duration of space flights (about 9 months max.)

10. Smart materials – adaptive growth

10.3 Adaptation strategies in wood

Wood is essentially dead tissue, grows by addition of material only (in the cambium underneath the bark).

No material removal or remodeling is possible!

Adaptation is possible by variation of composition, shape and structure of wood cell.

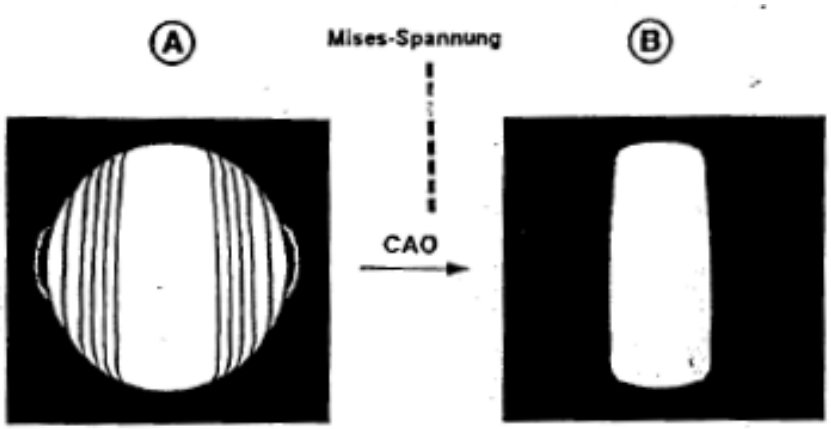
10. Smart materials – adaptive growth

Wound healing in trees

Like growth, also proceeds by adding material at cambium (beneath the bark).

Wounds of arbitrary shape tend to adopt longitudinal oval shape.

Modeling by CAO (computer aided optimization):
change in shape from round to oval leads to
decrease of Mises stress by 57%.



From Mattheck and Kubler, 1995

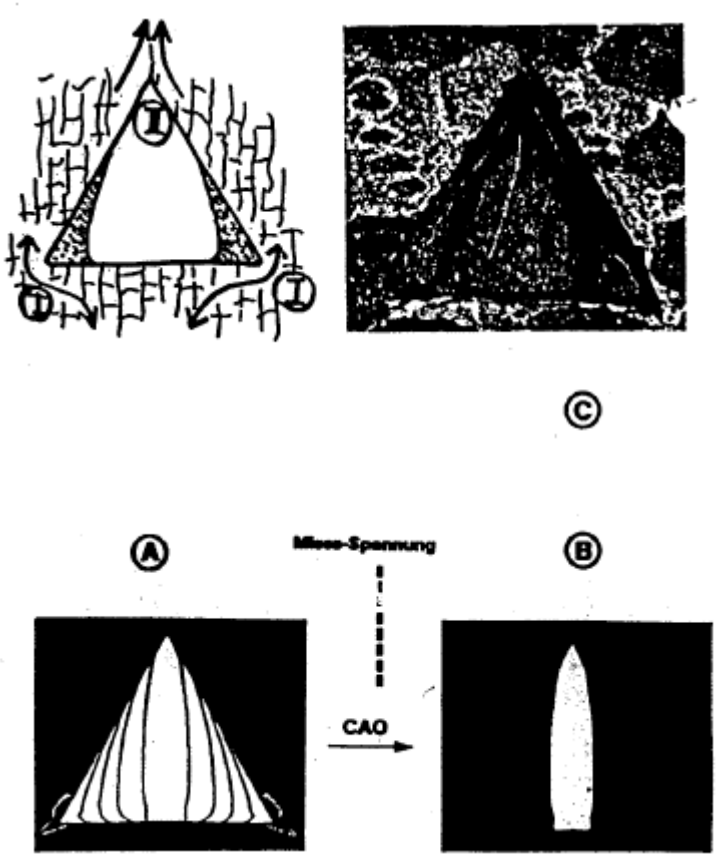
Example from real tree:

10. Smart materials – adaptive growth

Wound healing in trees

Example of triangular wound:

Change in shape from triangular to oval reduces Mises stress by 76%.

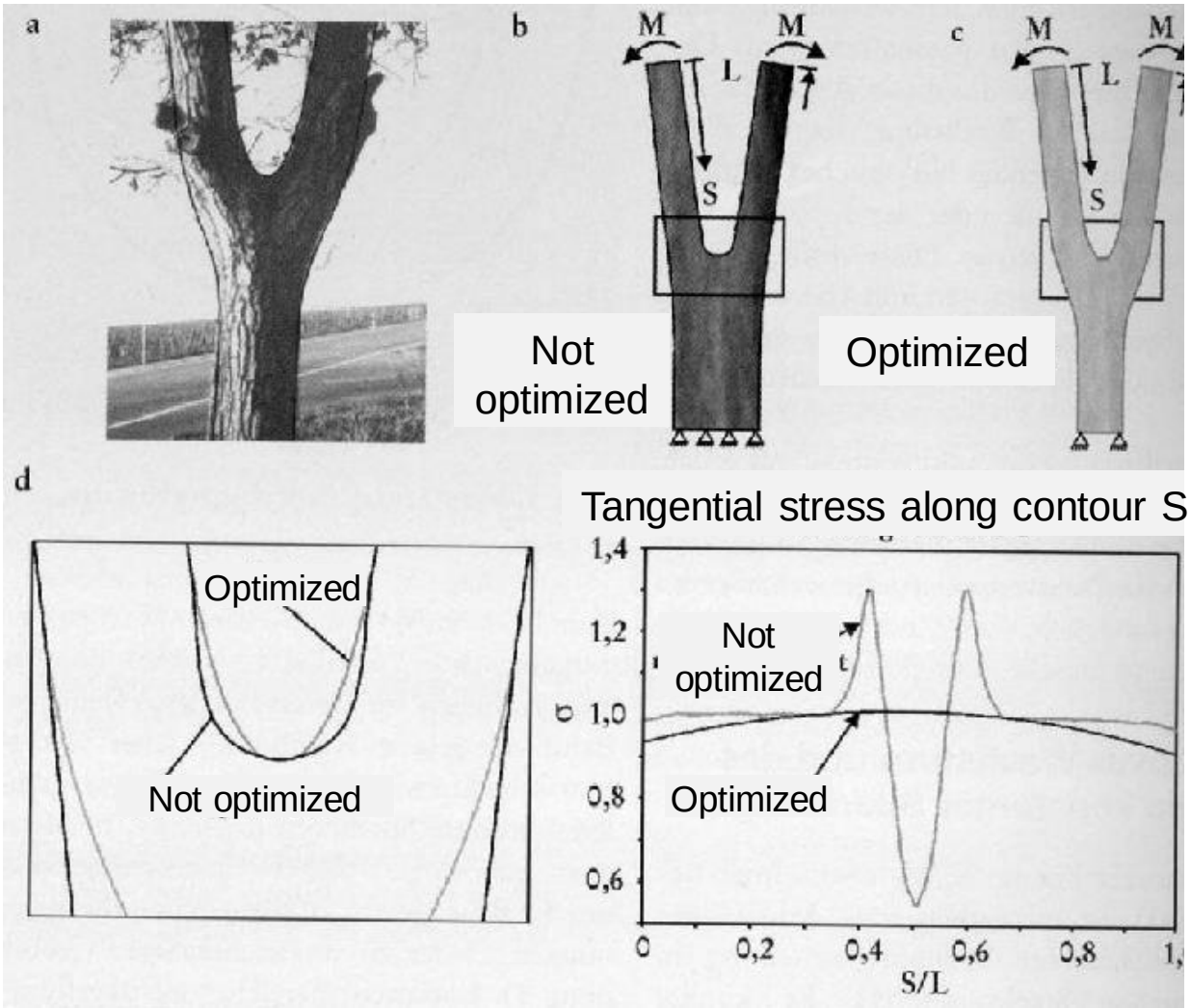


From Mattheck and Kubler, 1995

10. Smart materials – adaptive growth

Optimization of shape

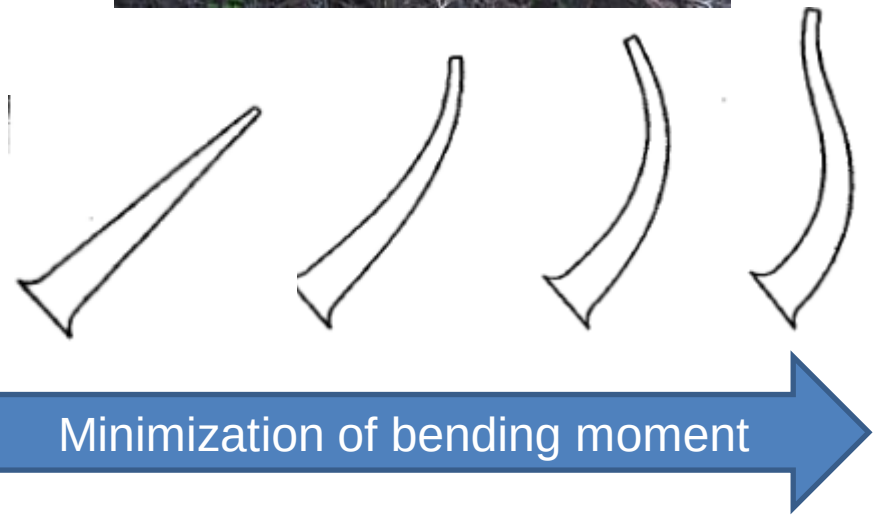
Branching of tree stem:



10. Smart materials – adaptive growth

Straightening of leaning stems

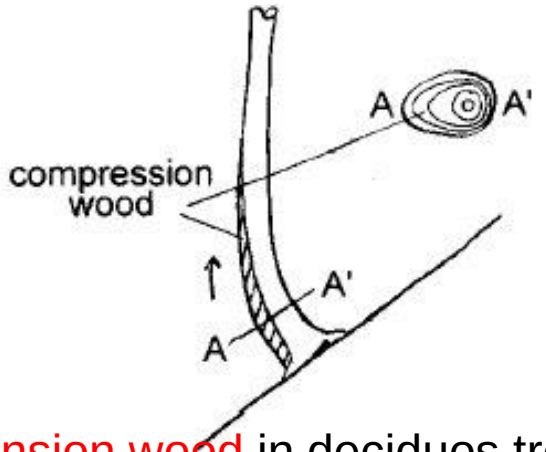
Minimizing bending loads acting on trunk and roots.



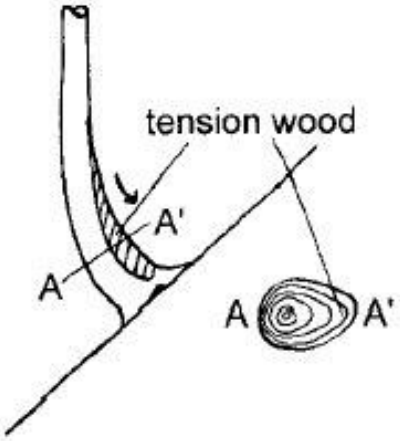
10. Smart materials – adaptive growth

Reaction wood

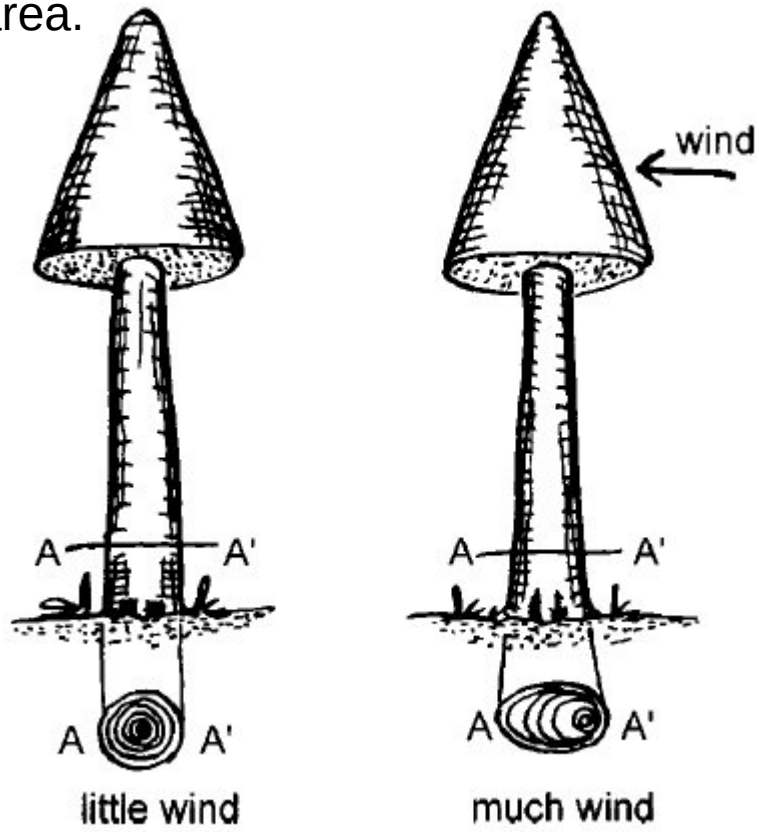
Compression wood in conifers (softwood)



Tension wood in deciduos trees (hardwood)



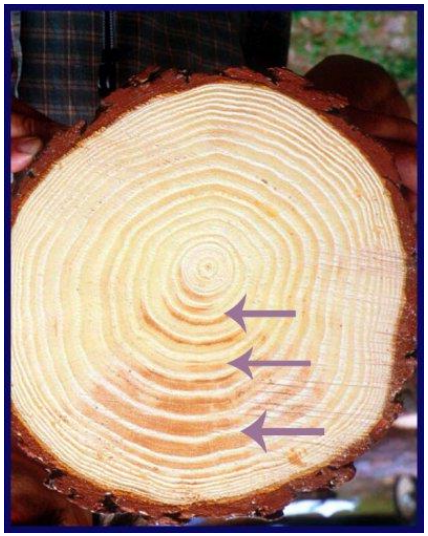
Schematic representation of formation of compression wood in conifer in windy area.



10. Smart materials – adaptive growth

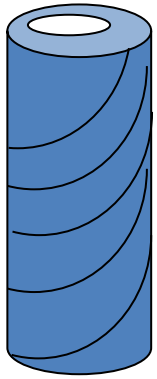
Compression wood

Reaction tissue, occurs in conifers. E.g. lower side of branch.



Nanostructure: large cellulose microfibril angle

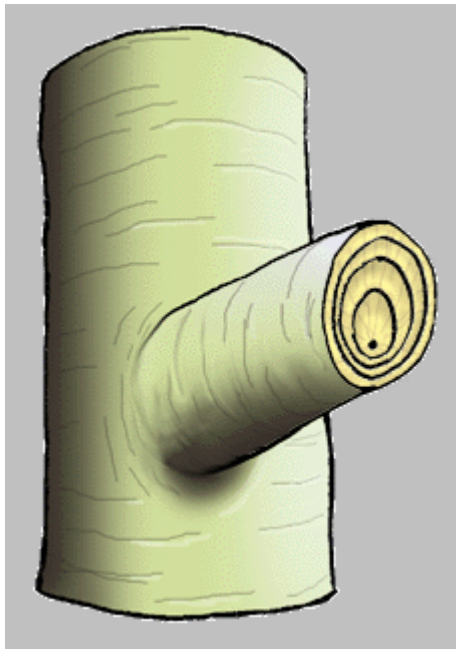
After deposition of cellulose wood is lignified. Compression wood contains high lignin content. Lignin spatially separates cellulose fibers → cells elongate and yield push-up effect.



10. Smart materials – adaptive growth

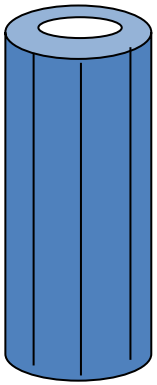
Tension wood

Reaction tissue, occurs in deciduous trees. E.g. upper side of branch.



Nanostructure: small cellulose microfibril angle

Cellulose fibrils are embedded in gelatineous layer that can swell upon hydration. Swelling separates cellulose fibers laterally, cells contract in longitundinal direction → pull-up effect



10. Smart materials – adaptive growth

Growing in of obstacles

Since trees cannot move, obstacles are grown in.

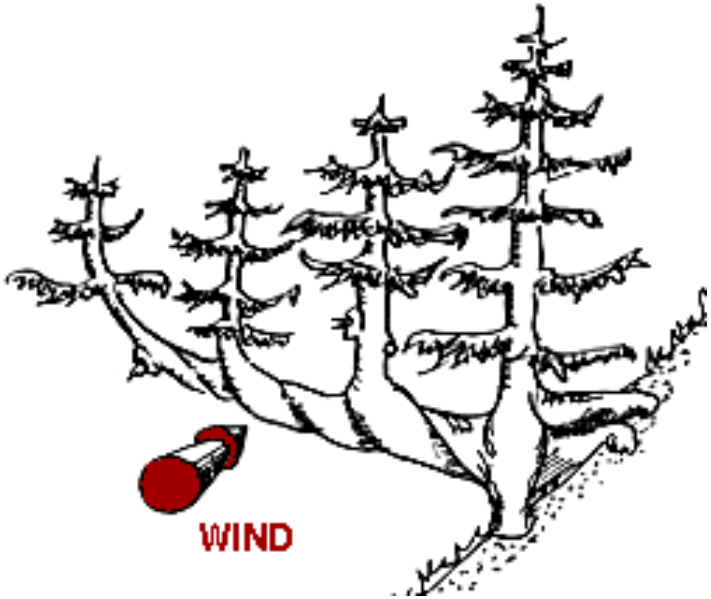
The contact area is enlarged to distribute the high contact stresses.

10. Smart materials – adaptive growth

Spiral growth

Special morphology found in trees from alpine or wind exposed sites.

Spirally arranged wood cells provide higher torsional rigidity than straight arrangement.



10. Smart materials – adaptive growth

Summary

Start design: safety factor depends on expected load conditions.

Adaptation of bone:

• Wound healing: spongy bone formed first, turns into cortical bone later, bone callus: over-reaction: more bone is formed than before to avoid another breakage;
• Bone responds to increased/decreased strain by adding/reducing bone mass
• Design adapted to load: trabeculae follow principal load directions (Wolff);
• Hip implants: exact fit is essential, problem of decreased load in upper part of femur;
• Osteoporosis: can occur in old age or due to missing strain (astronauts)

Adaptation of wood:

• Apdaptive growth only through selective addition of material (no remodeling);
• Goal: evenly distribute stress (avoid stress concentrations);
• Reaction to bending stresses (wind or gravity in leaning stems): growth of reaction wood (tension wood in deciduous trees, compression wood in conifers);
• Optimization to stiffness or flexibility through variations in ultrastructure

11. Biomimetic and bio-inspired materials

Biomimetics

Definition: Bio-mimetic = “imitating Nature”

History:

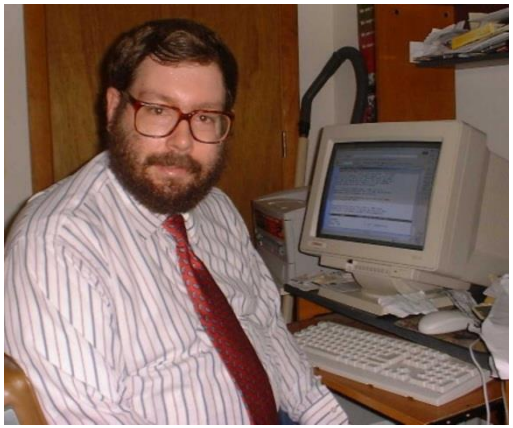
~ 1500 Leonardo da Vinci: flying apparatuses

~ 1890s Otto Lilienthal: first successful flight on a plane

since 1980s ever growing interest in biomimetic research

11. Biomimetic and bio-inspired materials

Technological progress



natural materials - modified natural materials - synthetic materials

So why look back to Nature?

11. Biomimetic and bio-inspired materials

What can we learn from biological materials?

Material properties

- trade-off between stiffness and toughness (bone)
- optimization on stiffness at low weight (wood)
- glue that works in dirty and wet environment (mussel glue)
- optimizing hardness and toughness by incorporation of organic additive (nacre)

etc.

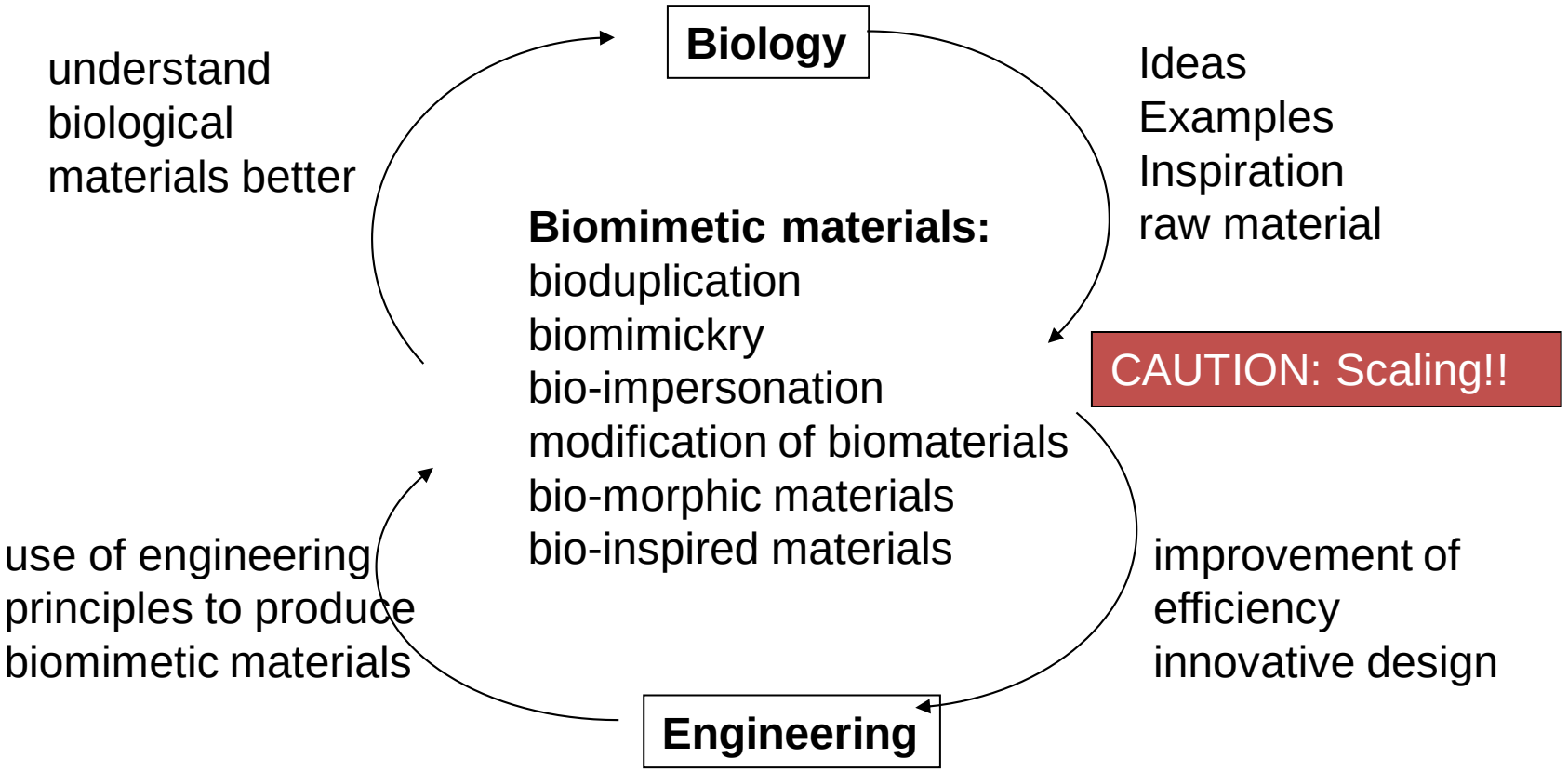
Processes and strategies

- add material where required and remove it where not required (smart, adaptive construction)
- self-healing, self-maintaining, self-repairing;
- capable of responding to environmental changes (sensing, feedback mechanism)

etc.

11. Biomimetic and bio-inspired materials

Biomimetic design



11. Biomimetic and bio-inspired materials

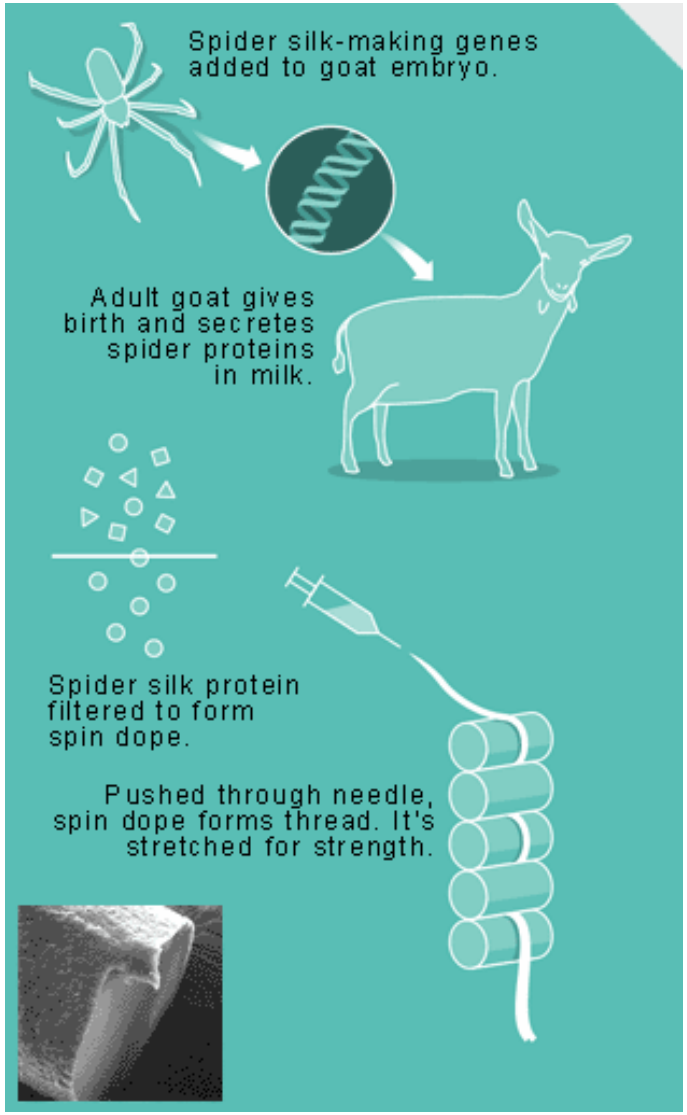
11.1 Biomimetic materials and structures

Bioduplication - Production of artificial spider silk.

- Dissolution and regeneration of natural silk.
- Recombinant production (genetic engineering)
  - DNA of various organisms is comined (molecular cloning)
  - Recombinant DNA introduced into host cell
  - If successful, also the foreign sections of genetic code will be expressed and corresponding protein synthesized.

11. Biomimetic and bio-inspired materials

Spider silk from goats



Genetically modified goats produce milk with spider silk proteins.

Proteins are isolated and spun into fibers in artificial spinning process.

Strength: approx. 20-40% of natural spider silk

11. Biomimetic and bio-inspired materials

Spider silk from goat milk

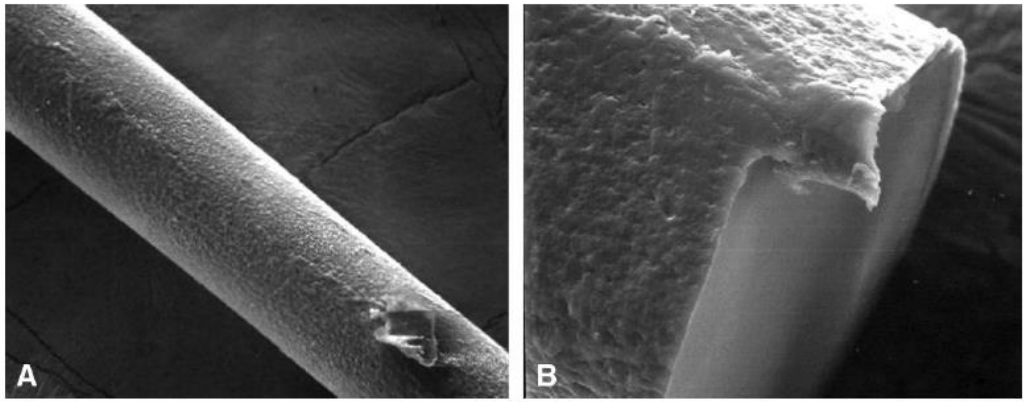


Fig. 7. Scanning electron micrographs of an ADF-3 as-spun fiber. (**A**) Analysis of fiber surface (magnification, ×500); (**B**) analysis at a break point to examine the fiber interior core (×2000).

Lazaris, A., *et al.*, *Science* (2002) **295**, 472–476

Sample	Draw	Draw ratio	Toughness (gpd)	Modulus (gpd)	% Strain break	Tenacity (gpd)	*n*
ADF-3, sample 1	M/W	5	0.895	42.8	59.6	1.91	7
ADF-3, sample-2	M/W	5	0.850	110.6	43.4	2.26	7
ADF-3, sample-3	M	4	0.645	63.2	45.0	1.8	5
Araneus, dragline	NA	NA	0.6–1.3	38–76	19–30	7–11	20

Was commercially exploited by Nexia Biotechnologies Inc. (Produkt „BioSteel“) in cooperation with US-army

Only very small amounts could be produced, bankruptcy in 2005

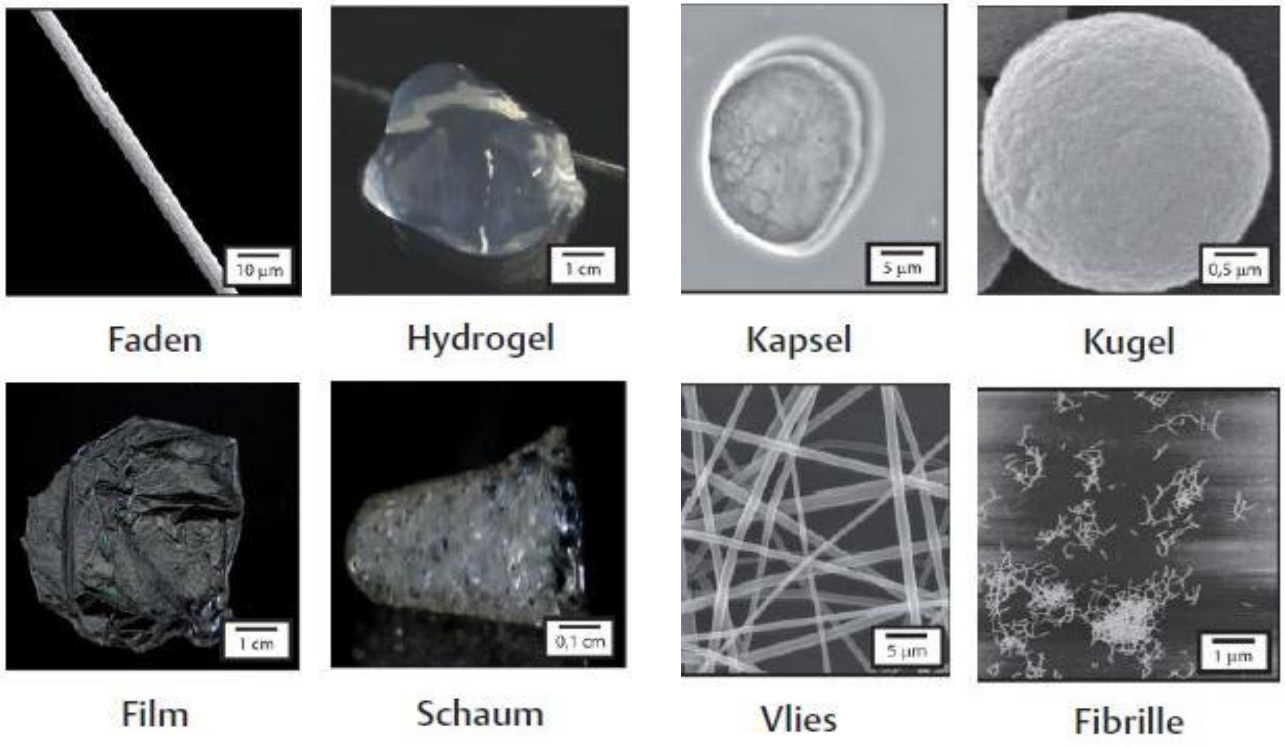
11. Biomimetic and bio-inspired materials

Recombinant spider silk from Escherichia coli bacteria

Produced by Amsilk, Spin-off of TU-München, founded in 2008

Offer various products, but no real high strength fibers, yet.

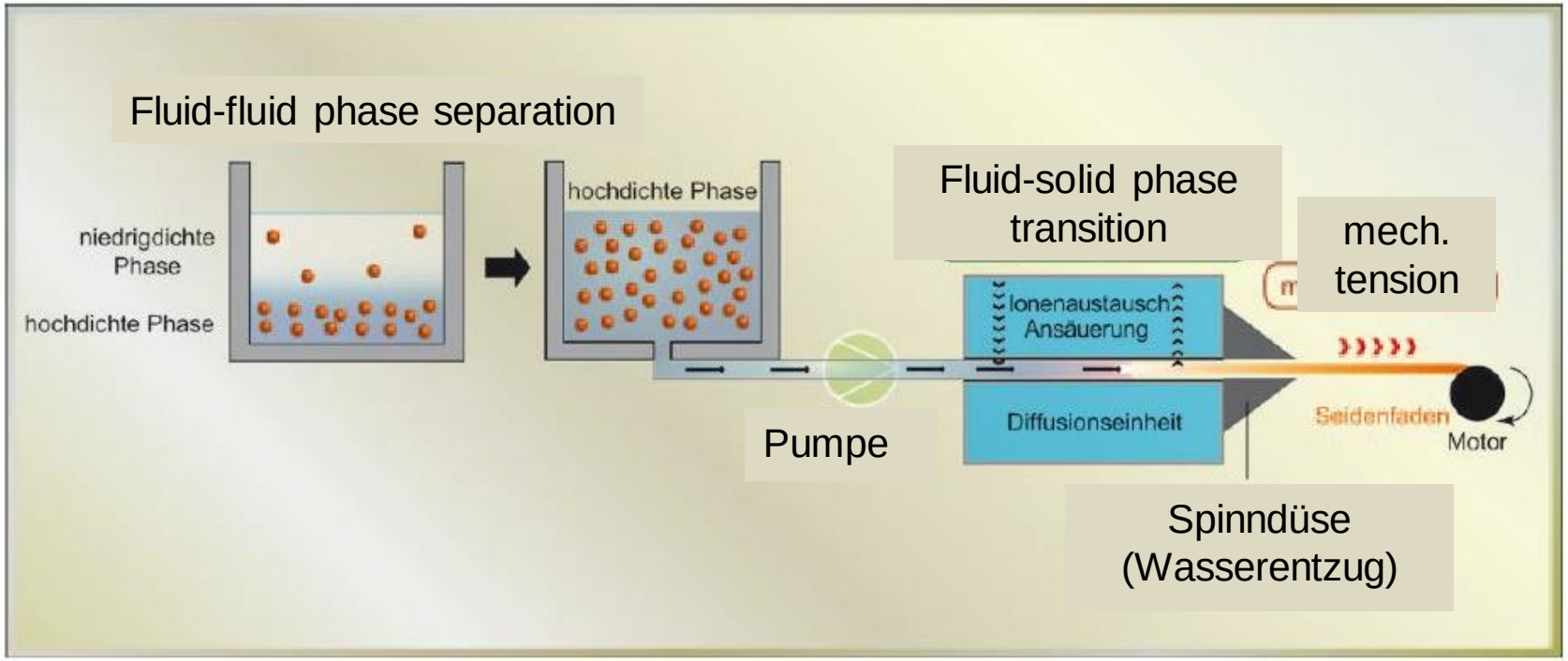
www.amsilk.com



Coin attached to AMSilk spider silk thread.

11. Biomimetic and bio-inspired materials

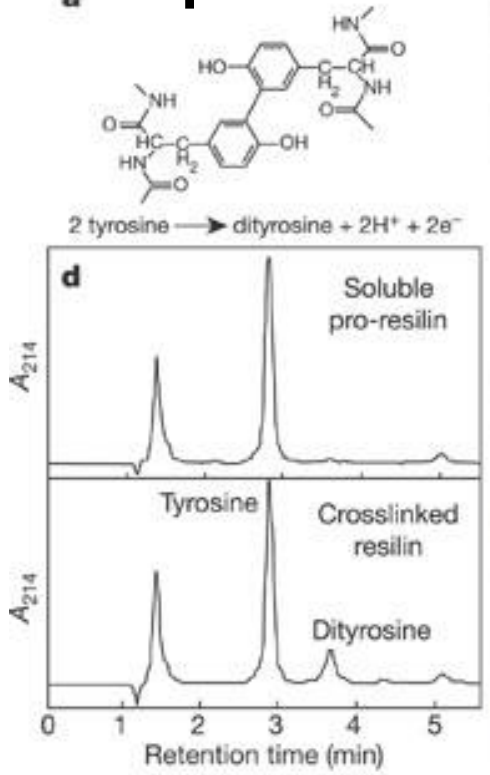
„Biomimetic“ spinning process

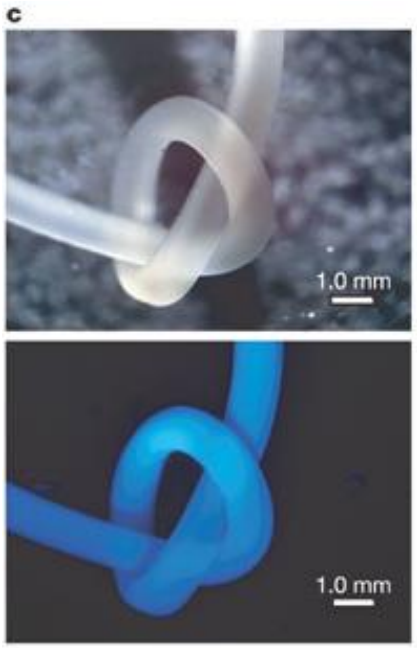


1. High density phase separated from low density phase.
2. High density phase pumped through diffusion unit.
3. Ion exchange and treatment with acid leads to fluid-solid phase transition
4. Pre-fabricated fiber is pulled from spinning duct → „strong“ fiber

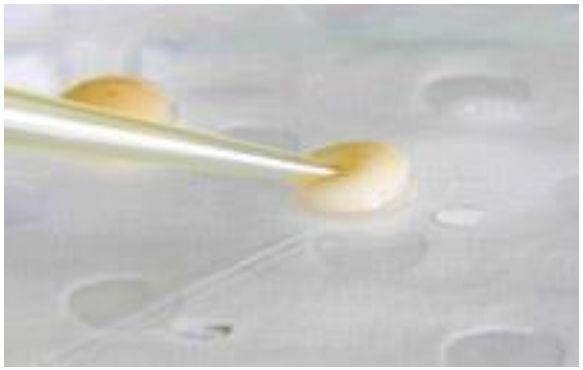
11. Biomimetic and bio-inspired materials

Bioduplication: synthesis of artificial resilin





Christopher Elvin, CSIRO, Australia
October 2005

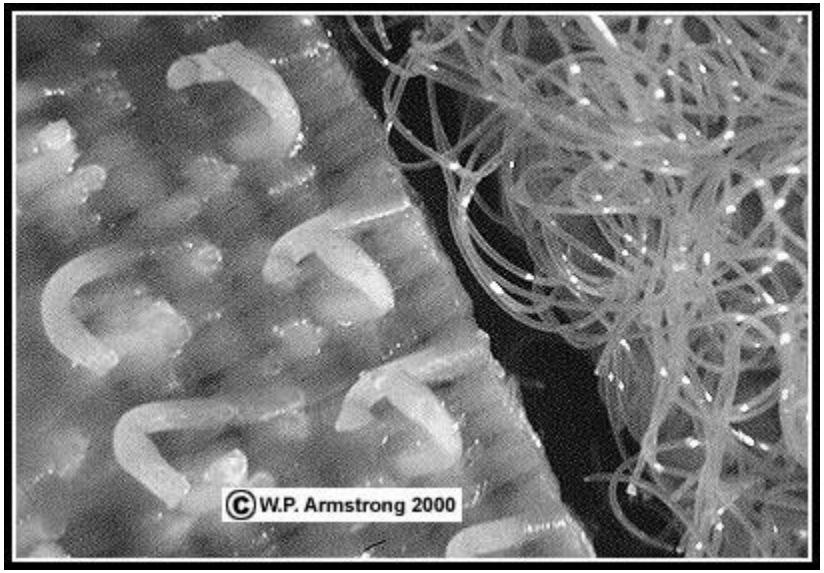


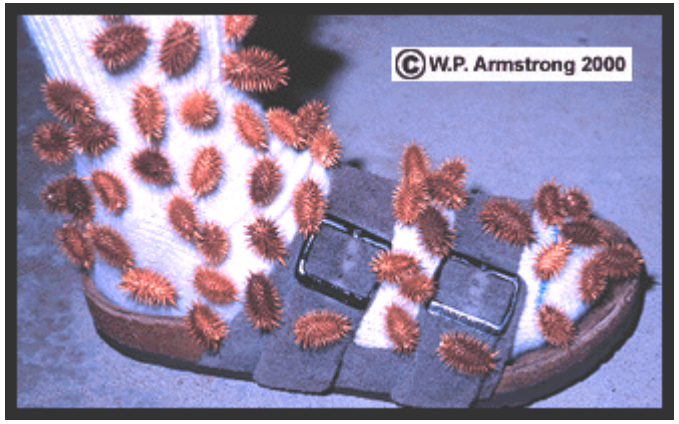
„The material has a similar resilience and long life to natural resilin, which can be stretched hundreds of millions of times without suffering wear and tear. The synthesised material is also superior to high-resilience polybutadiene rubber, used to make balls that bounce very high. And because resilin is similar to the human protein elastin, it could also be used as a so-called biomimetic material to replace worn out arteries or spinal discs.“

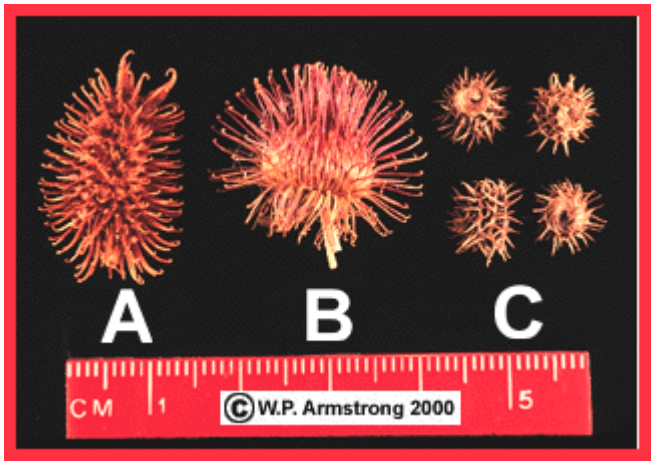
C.M. Elvin, et al. (2005). Synthesis and properties of crosslinked recombinant pro-resilin. Nature 437 (7051), 999-1002.

11. Biomimetic and bio-inspired materials

Bio-inspired systems, e.g. velcro







11. Biomimetic and bio-inspired materials

Lotus effect

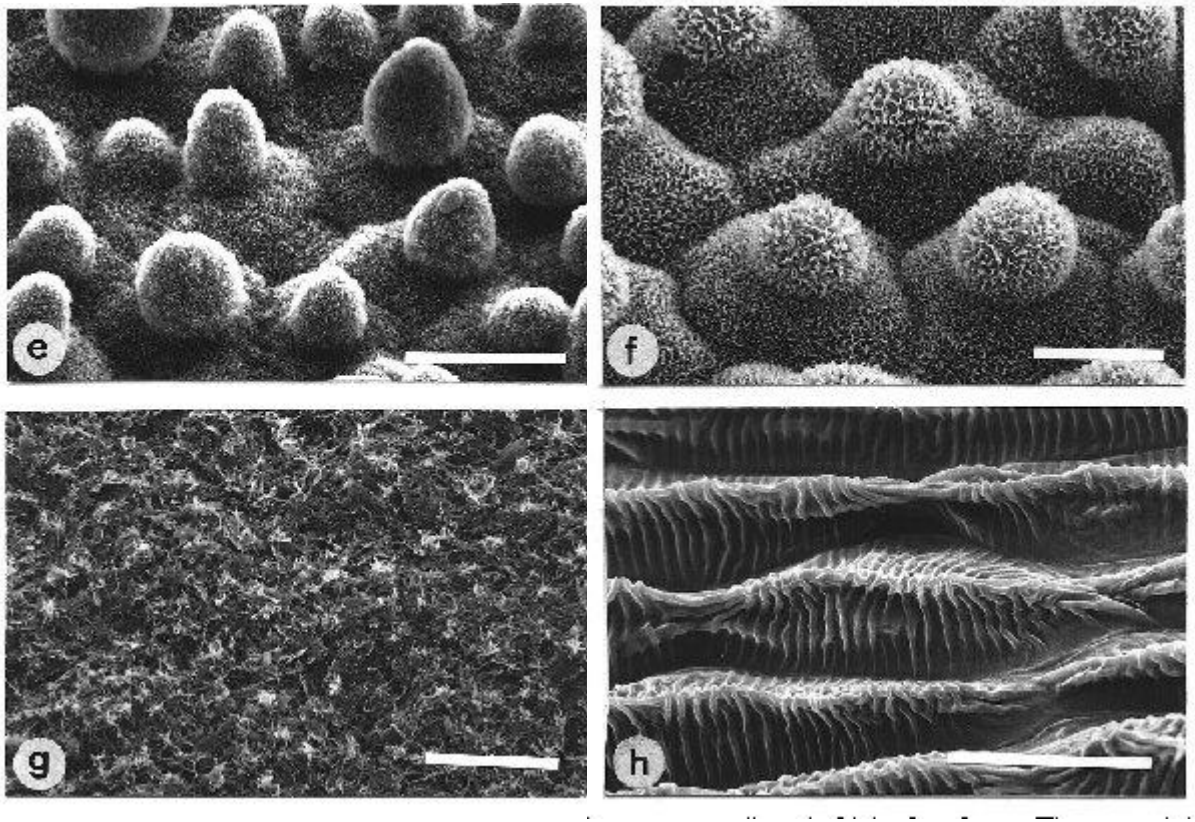
Lotus (and other plant leafs) are self-cleaning by nature. They repel water and dirt.

(e.g. Lotus is a symbol for puritiy in buddhism)

11. Biomimetic and bio-inspired materials

Lotus effect

Reason for lotus effect discovered in 1977 by botanist Wilhelm Barthloth: self cleaning is not due to super-smooth but super rough surfaces

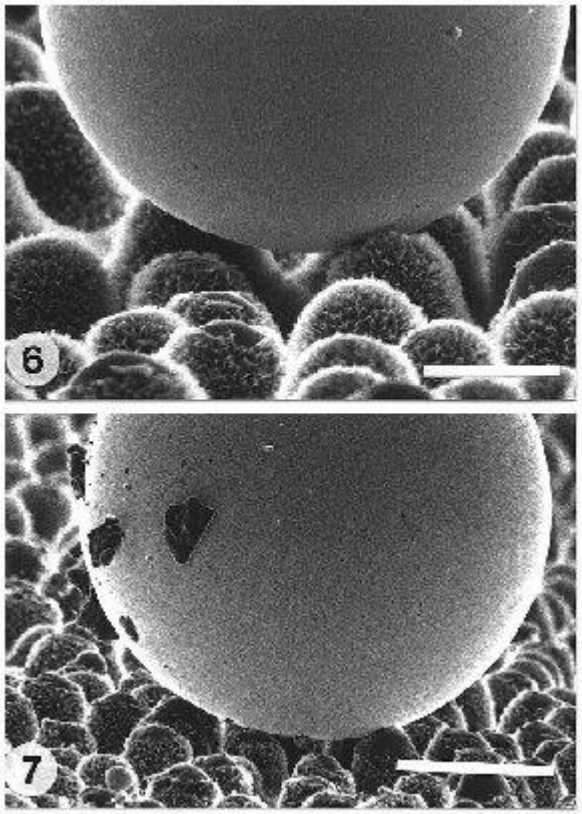


Water repellent, rough surfaces of the leafs of sacred lotus (*Nelumbo nucifera* Gaertn.), kohlrabi (*Brassica oleracea* L.), taro (*Colocasia esculenta* (L.) Schott.) and the petals of a composite (*Mutisia decurrens* Cav.).

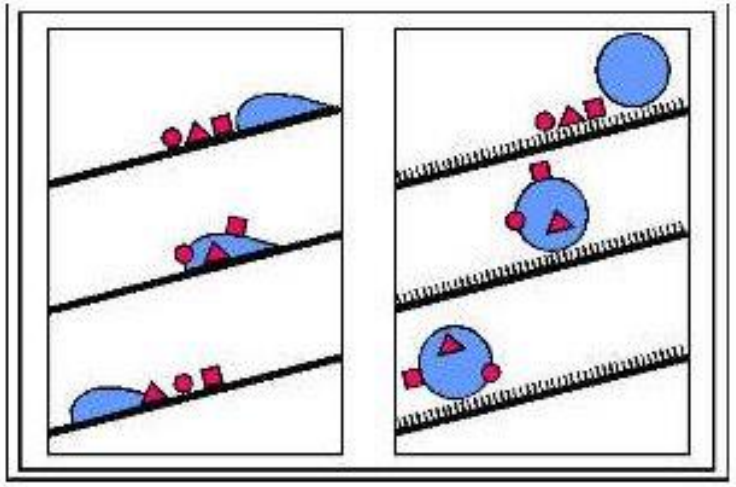
11. Biomimetic and bio-inspired materials

Principle of lotus effect

Surface tension of water is very high. Therefore it is energetically unfavorable to deform water surface to fill micro-and nano cavities.



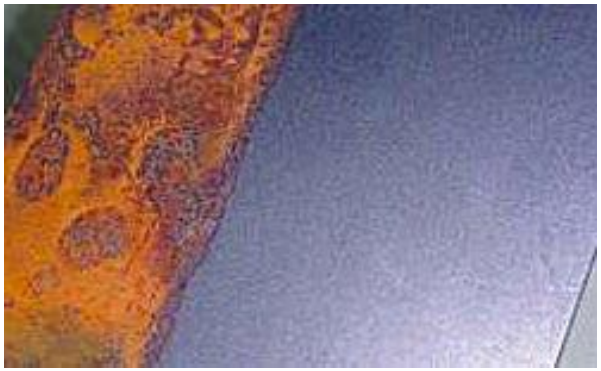
Self-cleaning effect:
Dirt is taken up by water droplet. On conventional surface deposited again, on lotus-like surface no wetting and dirt is carried away.



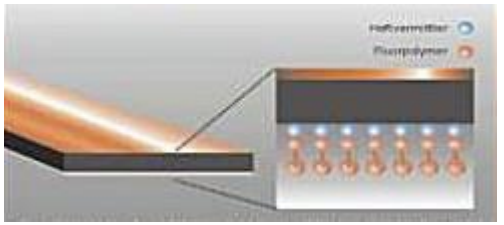
11. Biomimetic and bio-inspired materials

Applications of the lotus effect

Car polish: self cleaning



Metal: Protection against corrosion



Ski-wax: less friction on snow

Windshield: no need for windshield wipers any more

Self cleaning paint

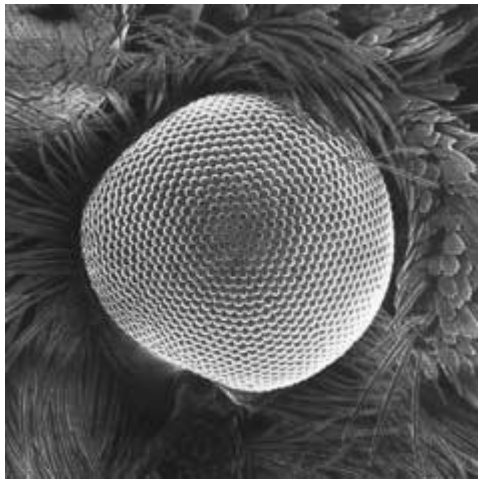
11. Biomimetic and bio-inspired materials

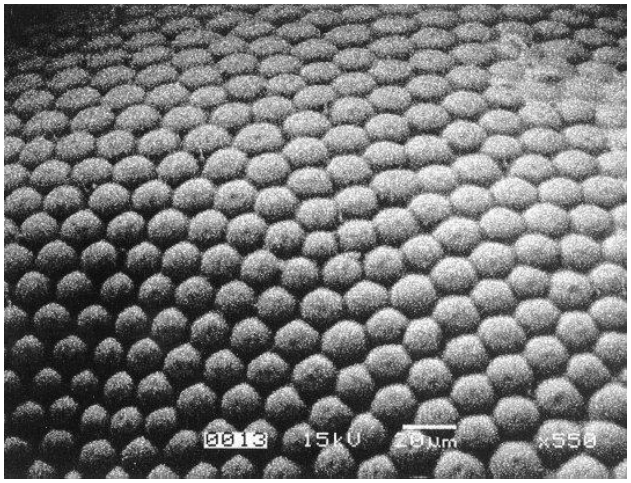
Moth eye

To see, but not to be seen.

Surface structure minimizes reflections

- Increase amount of light entering the eye
- Minimizing the risk to be seen by a predator.

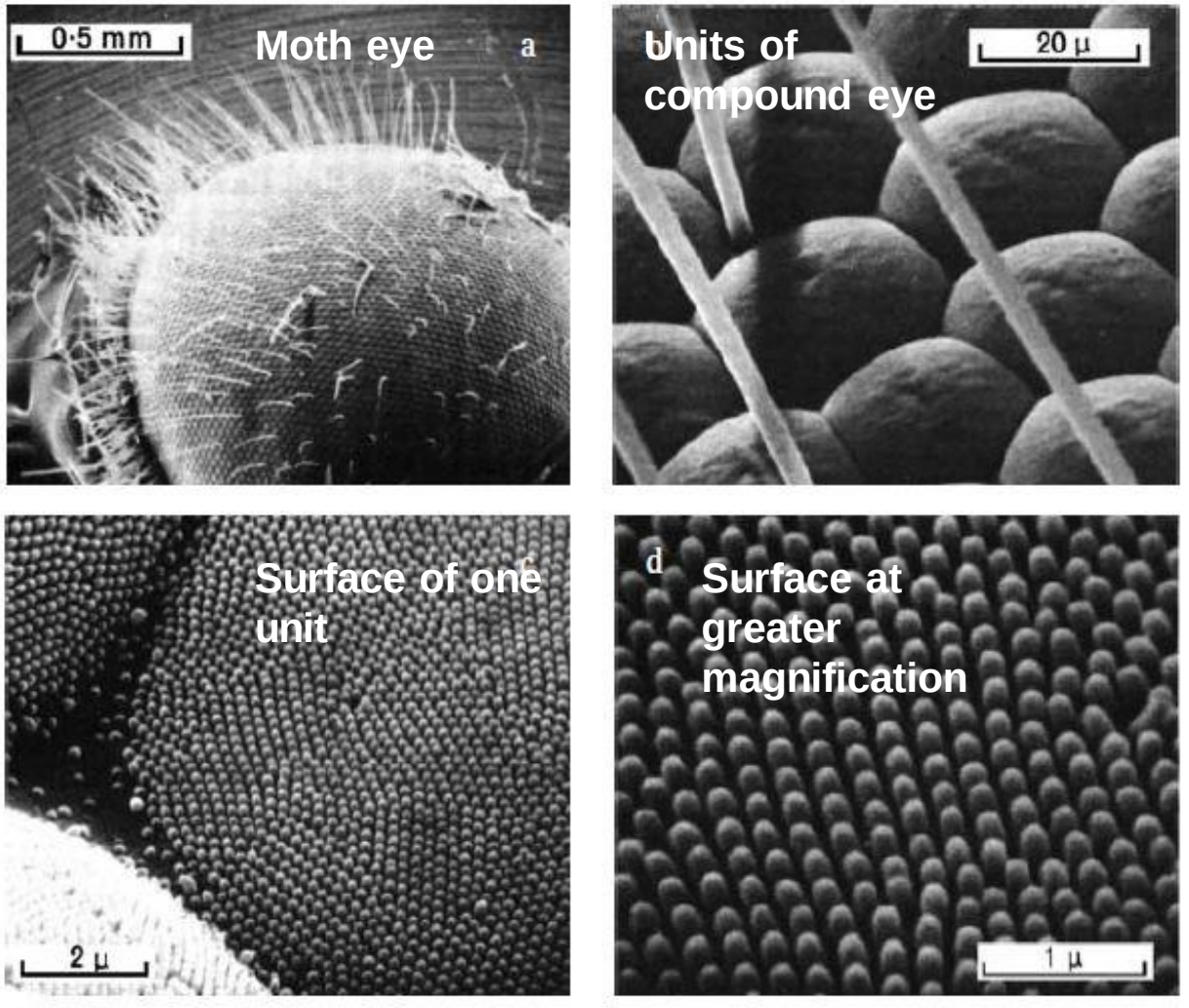




11. Biomimetic and bio-inspired materials

Moth eye

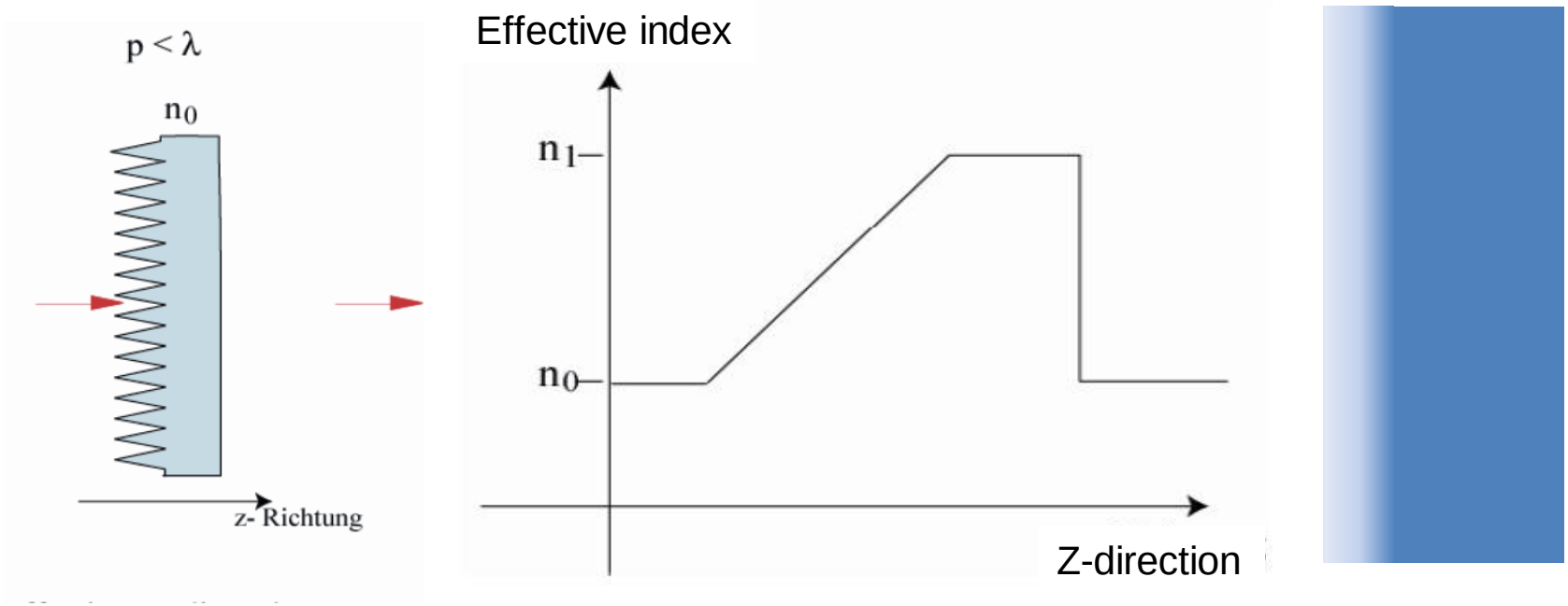
Antireflective properties were discoverd in 1960s by C. G. Bernhard *(Endeavour 26, 79- 84, 1967)*



11. Biomimetic and bio-inspired materials

Principle of antireflective properties in moth eyes

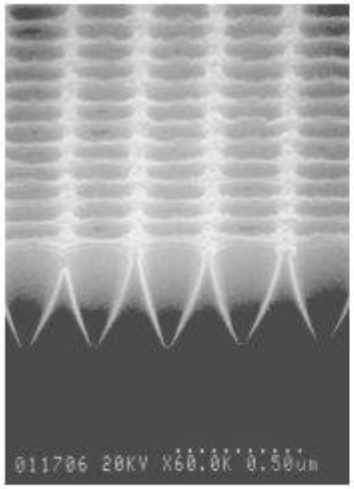
Small structures cause incident light to “see” a refractive index gradient.

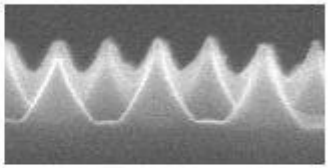


Effective medium theory: predicts that for structural elements smaller than the wavelength of light (in moth eye about 200 nm), no diffraction will take place but elements act like a continuum with effective refractive index.

11. Biomimetic and bio-inspired materials

Applications: anti-reflective coating of solar panels



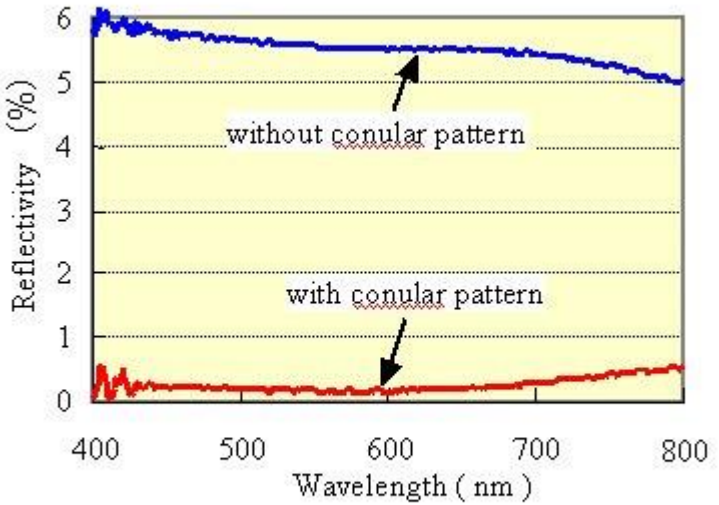


Curvature

Convex

Product Name:
Moth Eye Anti-reflective Nano-structure

Specifications:



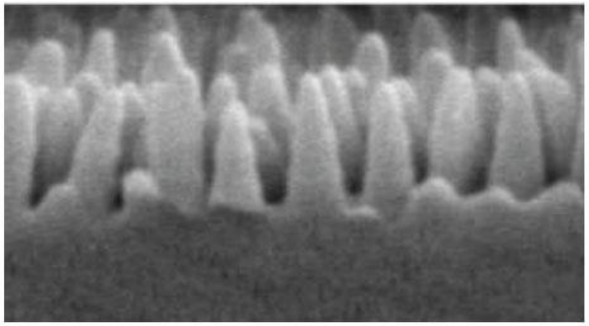
Reflectivity of plastic surface molded by the master block

coating for solar panels

11. Biomimetic and bio-inspired materials

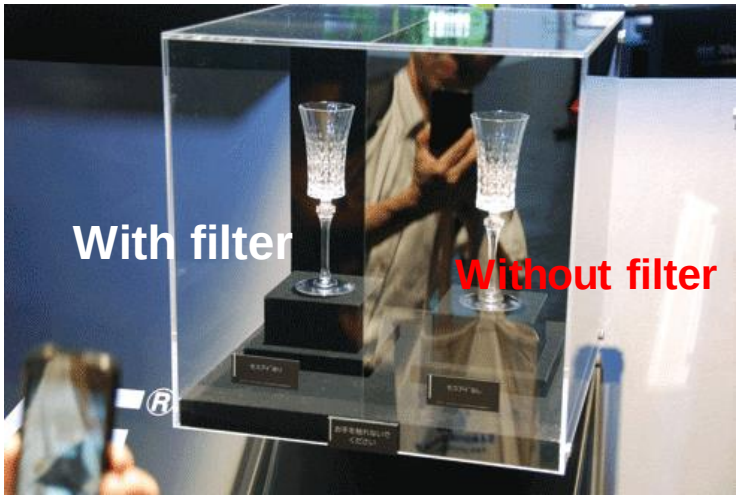
Antireflective coating of TV screens

z.B. **Philips** 9000er Smart LED-TVs by Philips, 2011, with „moth eye filter“



Surface of Philips moth eye filter

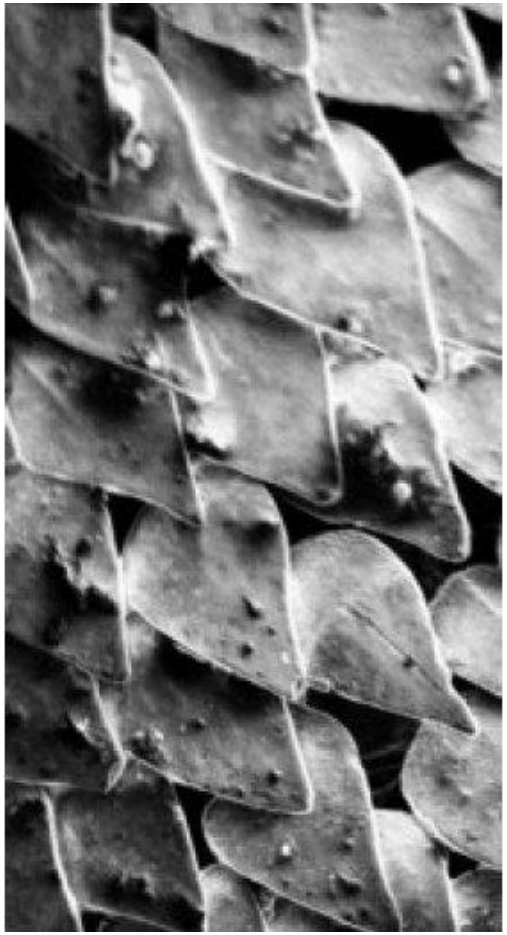
Sharp announced Big Aquos TV screen with moth eye technology (Oct. 2012)



Sharp moth eye filter demo

11. Biomimetic and bio-inspired materials

Shark skin



Shark skin, electron microscopy.
Skin covered with dermal denticles (same material as teeth).

Technological applications:

- reduce drag on flat surfaces on ships and aircrafts

- swim suits:
Speedo, *Fastskin,* worn at Sydney Olympics 2000 by 27 of the 33 gold medalists

source: http://www.extra.rdg.ac.uk/eng/BIONIS/

11. Biomimetic and bio-inspired materials

11.2 Bio-inspired processes

Bio-inspired mineralization

- Combination of mineral and bio-macromolecules in solution
- Control of environmental conditions (temperature, pH).
- Precipitation and crystallization of mineral is controlled by macromolecules.

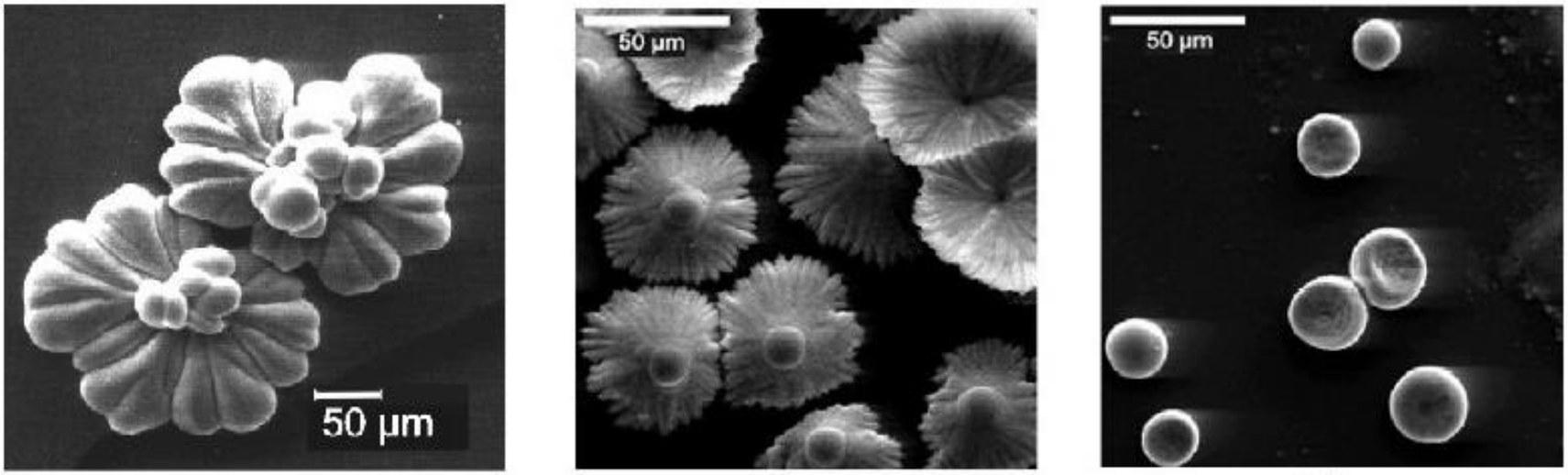


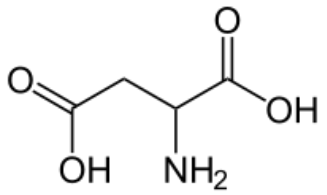
Fig. 4. Control of complex $CaCO_3$ nanoparticle superstructures with block copolymers exhibiting a from left to right increasing surface activity. PEG_{45}–PGL_{27} 100% phosphorylated (a), PEG_{84}–$PHEE_{13}$ with 40% (b) and 10% (c) phosphorylation degree. PEG, poly(ethylene glycol); PGL, poly(glycidol); PHEE, poly(hydroxyethyl ethylene). Reproduced from Rudloff et al. [23•] with permission.

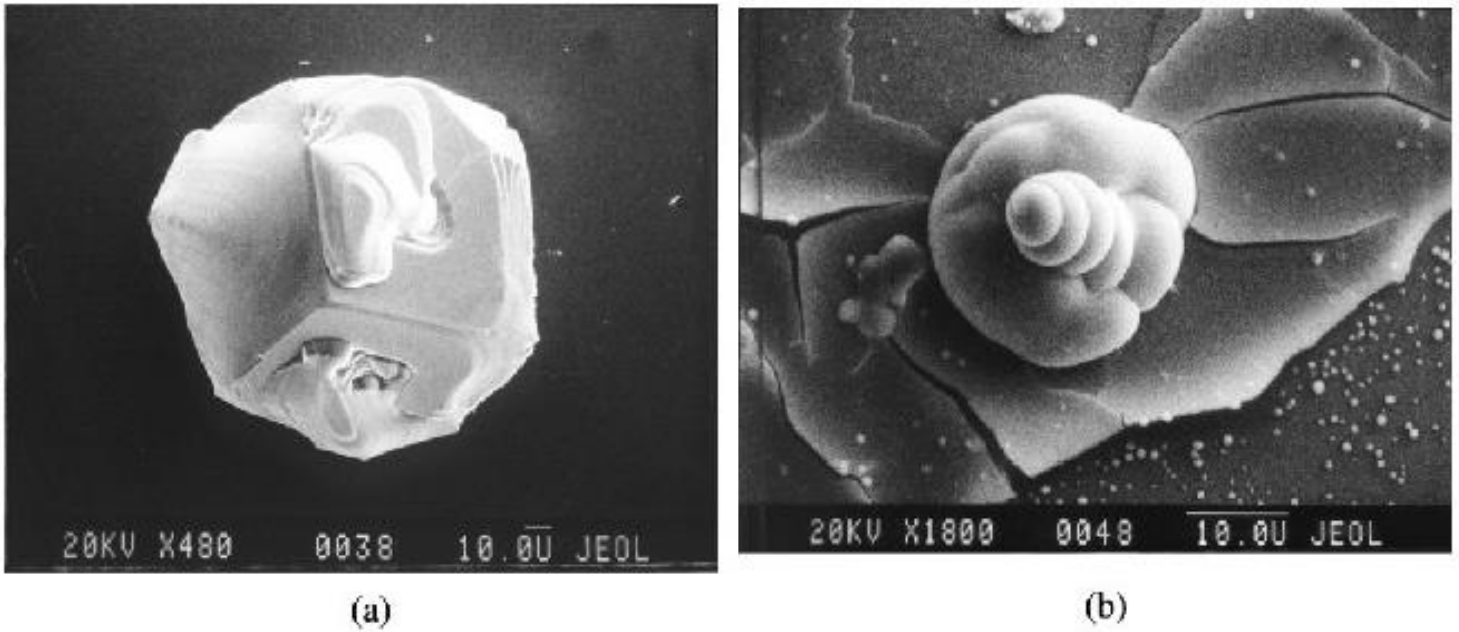
H. Cölfen, *Current Opinion in Colloid & Interface Science* 8 (1), 23-31 (2003).

11. Biomimetic and bio-inspired materials

Bio-inspired mineralization

Production of oriented, helical mineral structures through the influence of macromolecules with intrinsic directionality (Poly-Aspartate)



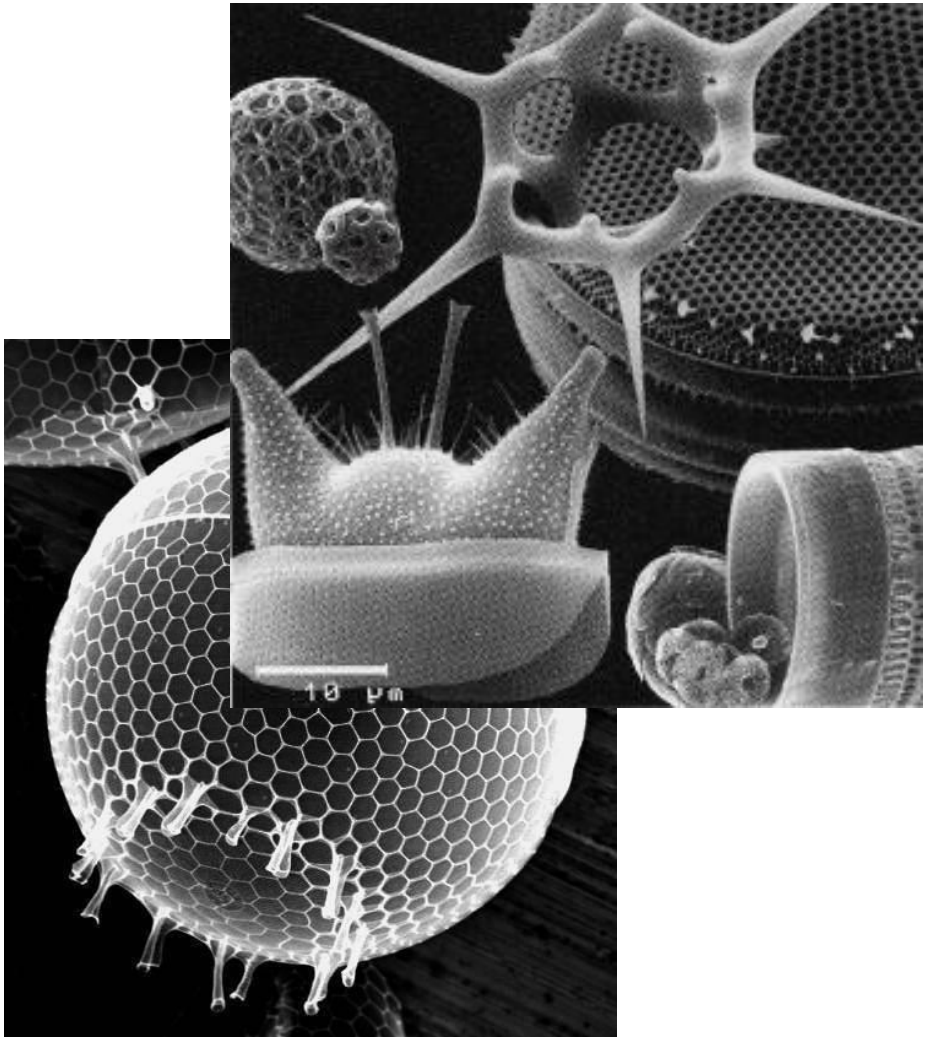


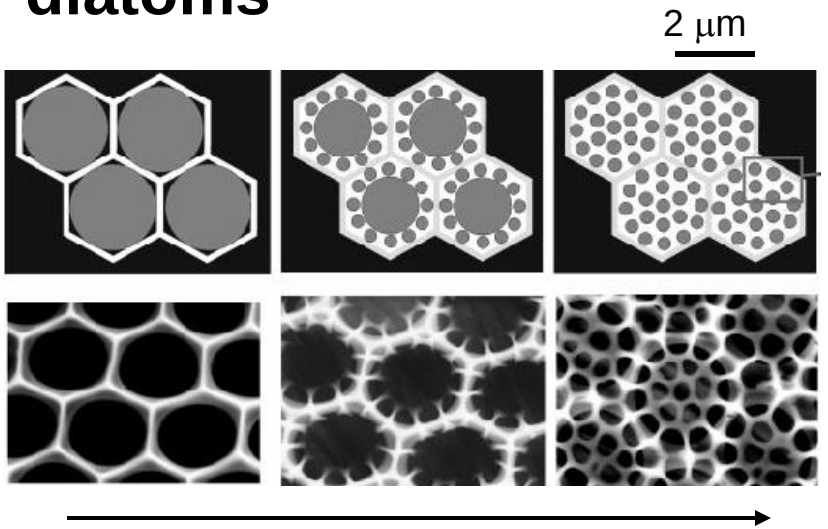
(a) (b)

Fig. 5. Distorted calcite crystals with 'molten' appearance (a) and vaterite aggregates with helical protrusions formed by a PILP process with a polyaspartic acid additive. Reproduced from Gower and Odom [30••] with permission.

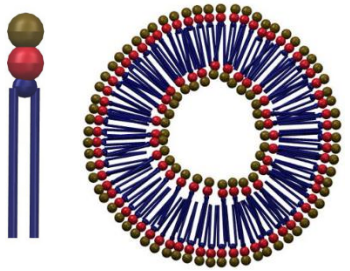
11. Biomimetic and bio-inspired materials

Porous structures inspired by diatoms





Coscinodiscus wailesii



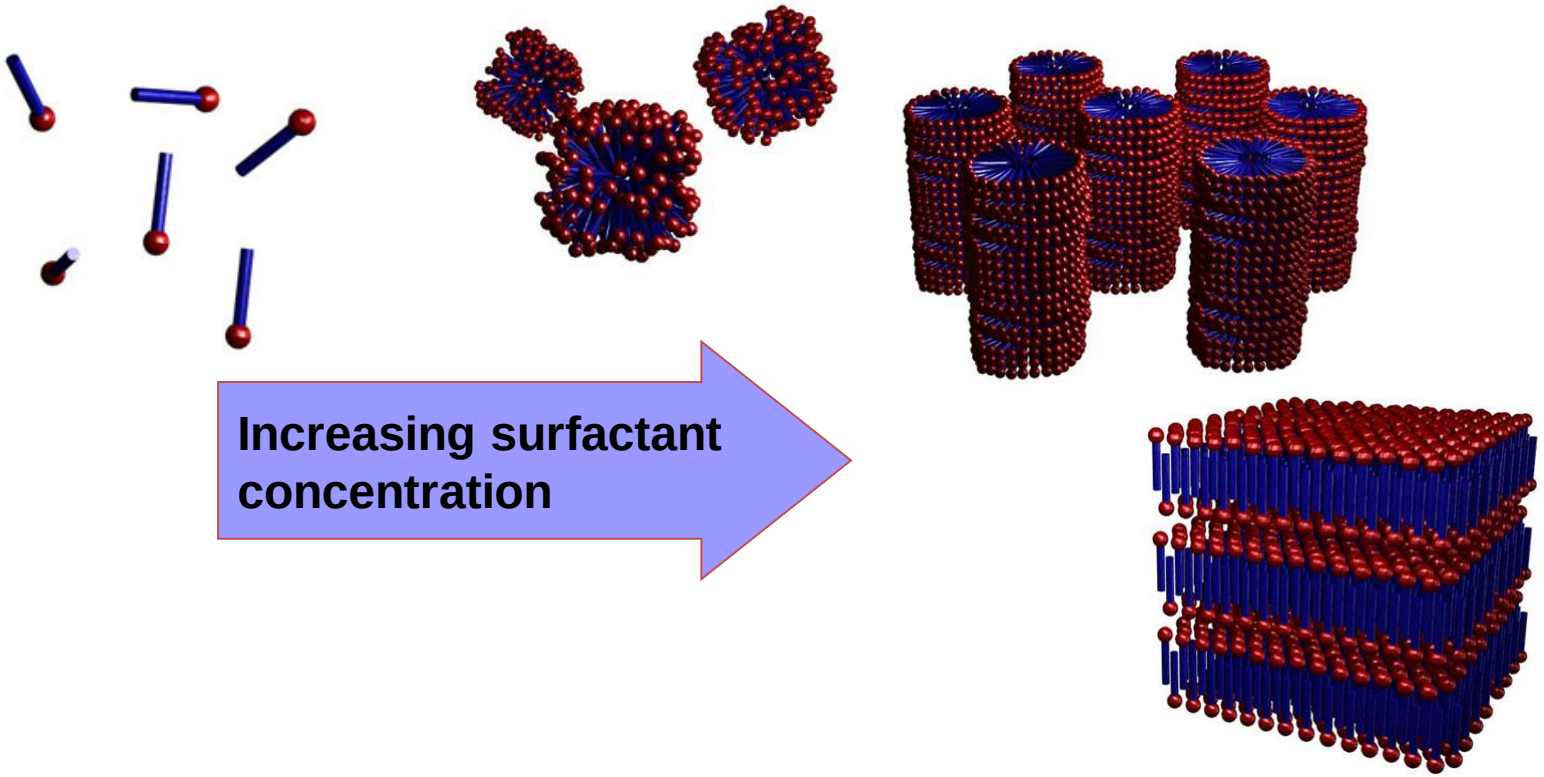
vesicle

M. Sumper (2002). *Science* **295**(5564), 2430-2433.

11. Biomimetic and bio-inspired materials

Self-assembly of surfactants in water

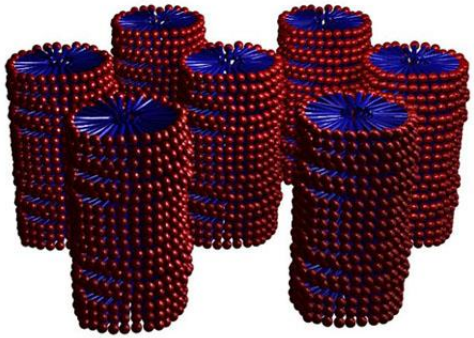
- By choice of suitabel surfactant and variation of concentration, different structures may be achieved.



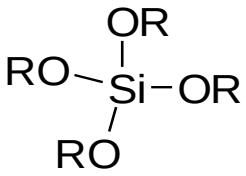
11. Biomimetic and bio-inspired materials

Mesoporöse materials via sol-gel process

Liquid crystalline



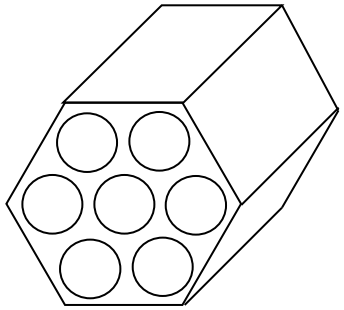
+



Inorganic precursor

Sol-gel process

Remove surfactant with heat treatment



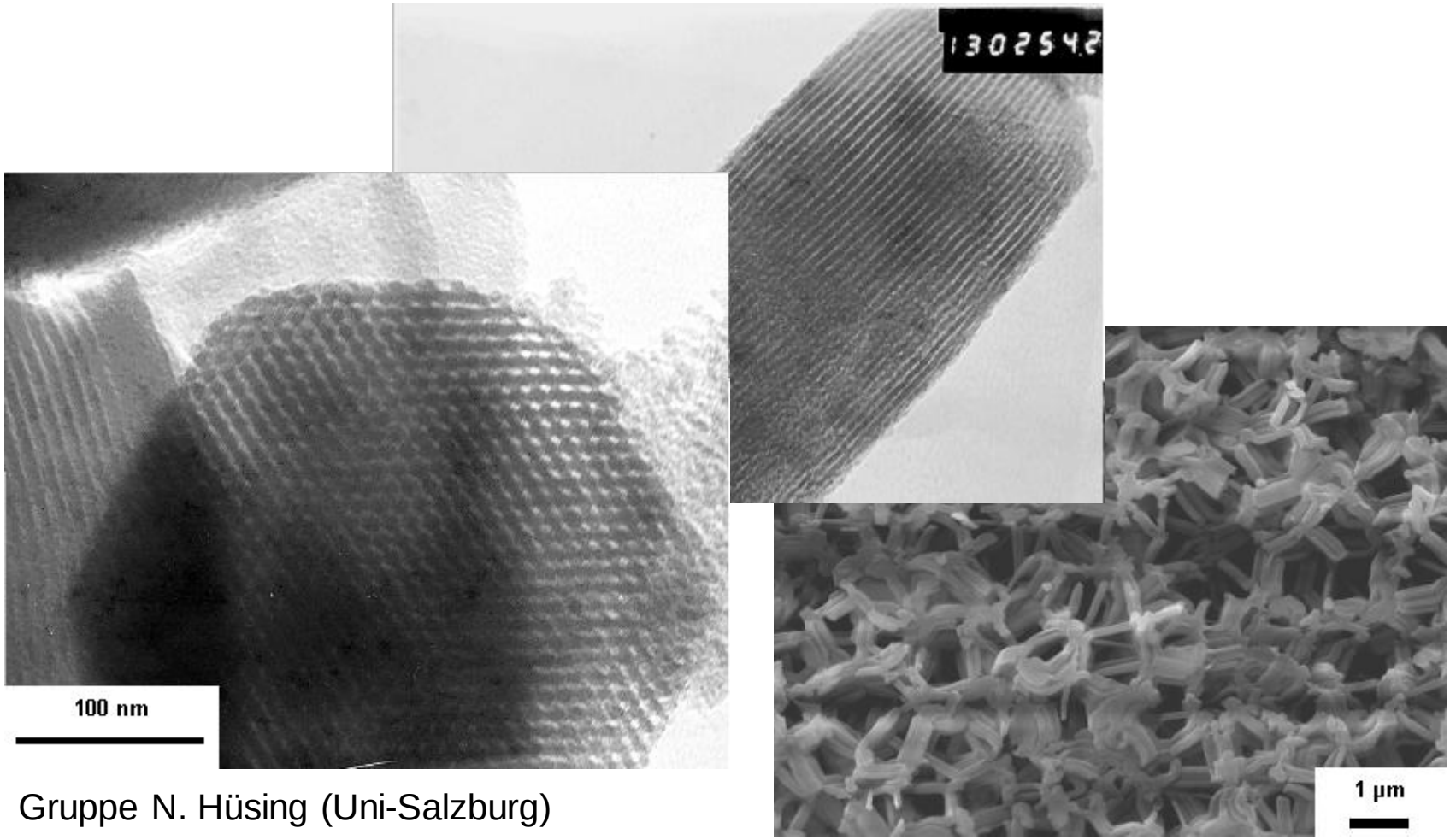
SiO_2 with ordered mesopores

(here: hexagonal)

See also Kresge et al. *Nature*, 1992, *359*, 710.

11. Biomimetic and bio-inspired materials

Example: hierarchically structured porous Silica



Gruppe N. Hüsing (Uni-Salzburg)

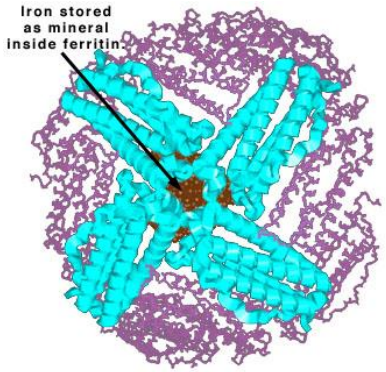
Applications: filters, catalysts, gas chromatography

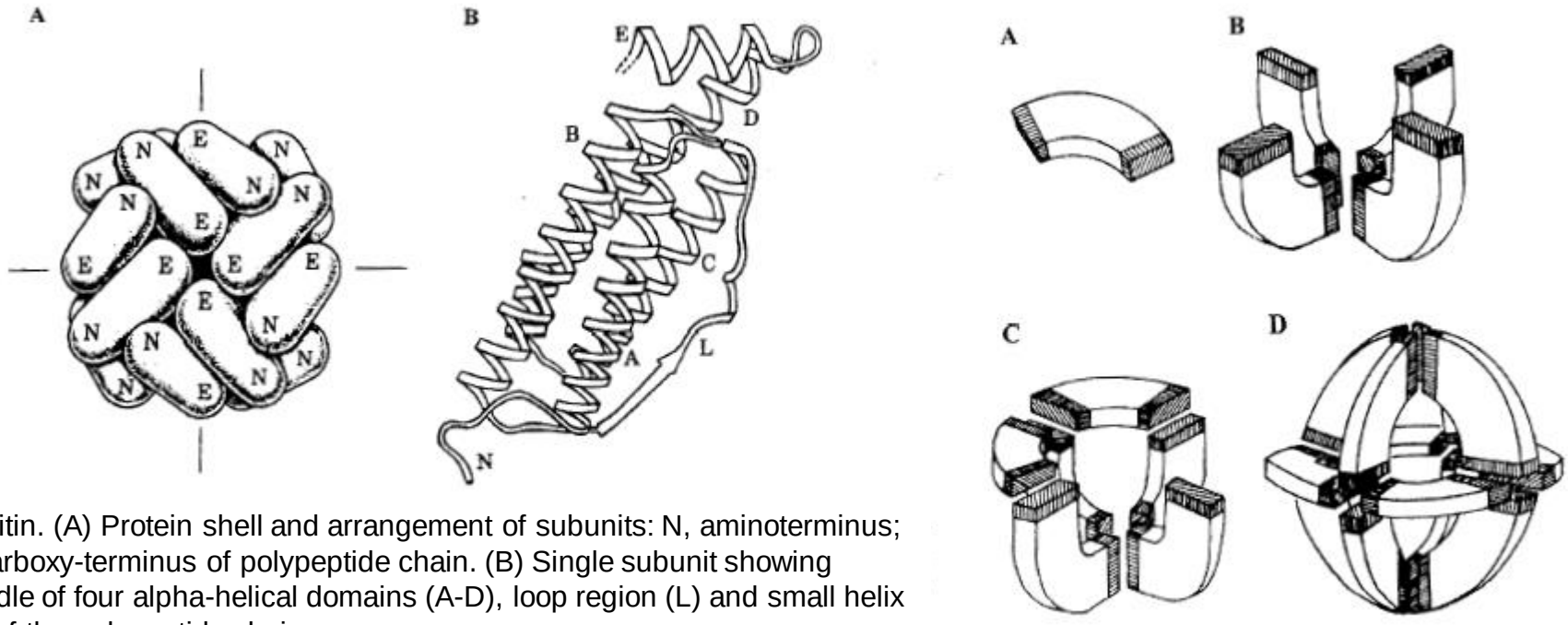
11. Biomimetic and bio-inspired materials

Bio-templated nanoparticles

e.g. based on iron storage protein ferritin

8 hydrophilic and 6 hydrophobic pores, core: ferrihydrite („rust“)



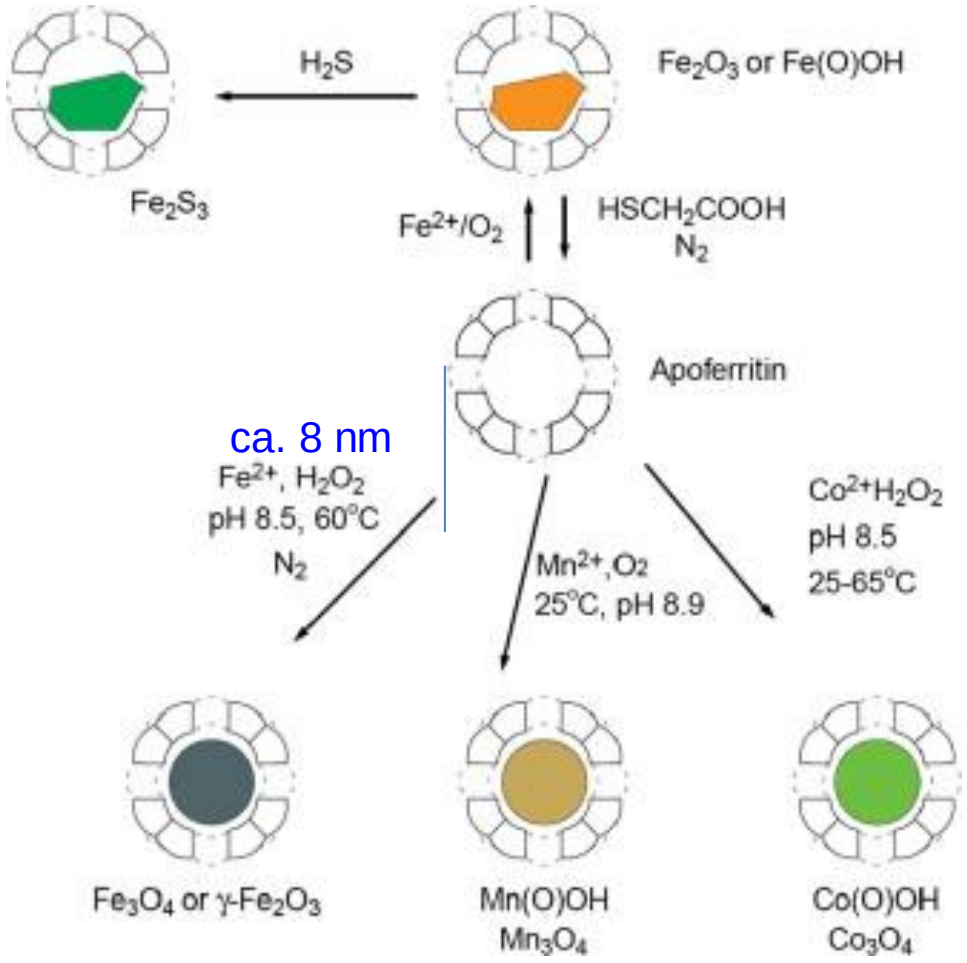


Ferritin. (A) Protein shell and arrangement of subunits: N, aminoterminus; E carboxy-terminus of polypeptide chain. (B) Single subunit showing bundle of four alpha-helical domains (A-D), loop region (L) and small helix (E) of the polypeptide chain.

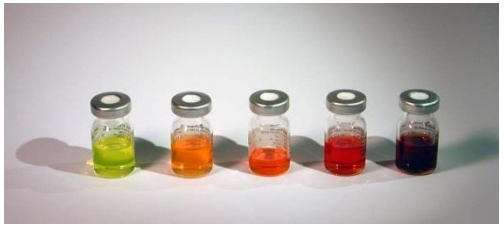
11. Biomimetic and bio-inspired materials

Nanoparticles from ferritin

Production of nanoparticles with defined size from apoferritin (empty ferritin)



e.g. CdSe quantum dots (quantum dots absorb light and re-emit it in different color, depending on size)



Fan et al. (2009) Prog. Mat. Sci 54(5), 542-659

11. Biomimetic and bio-inspired materials

Imitating muscle motion

Muscle movement:

triggered by a weak electric pulse arriving from the brain through nerves which promotes an increase of Ca+2 ion concentration inside the myofibrils from 10^{-7} to 10^{-3} M.

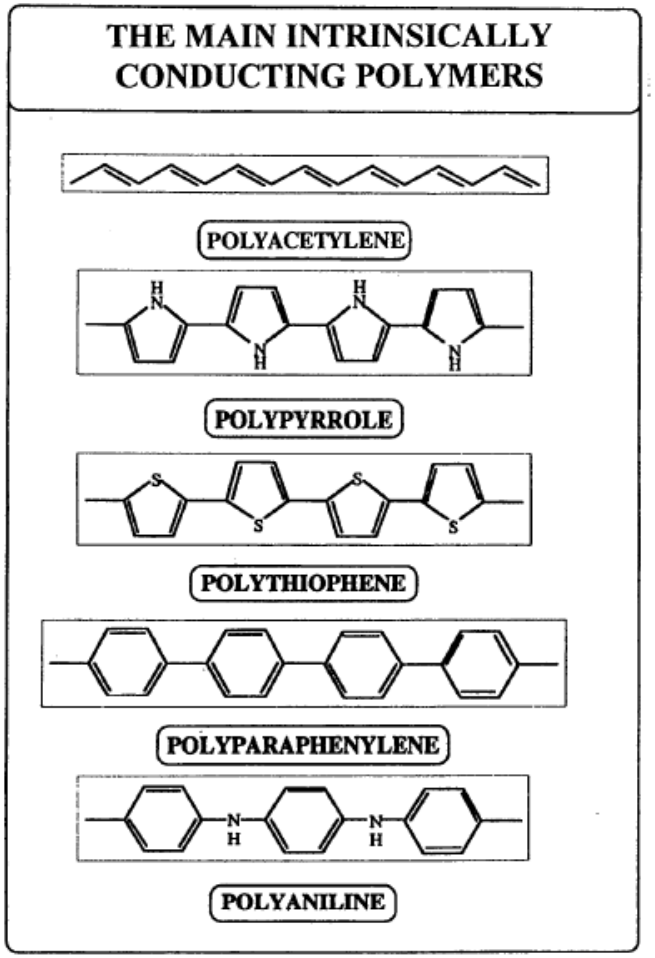
Conformational changes in the troponim-tropomyosin system allow muscle to contract.

Historical discovery: Galvani‘s experiment with frog‘s leg

11. Biomimetic and bio-inspired materials

Conducting polymers for movement

Discovery of polymers that do not behave as insulators but rather like metals conducting electrical current.



The Nobel Prize in Chemistry 2000

"for the discovery and development of conductive polymers"

Alan J. Heeger

1/3 of the prize

USA

University of California Santa Barbara, CA, USA

b. 1936

Alan G. MacDiarmid

1/3 of the prize

USA and New Zealand

University of Pennsylvania Philadelphia, PA, USA

b. 1927 (in Masterton, New Zealand)

Hideki Shirakawa

1/3 of the prize

Japan

University of Tsukuba Tokyo, Japan

b. 1936

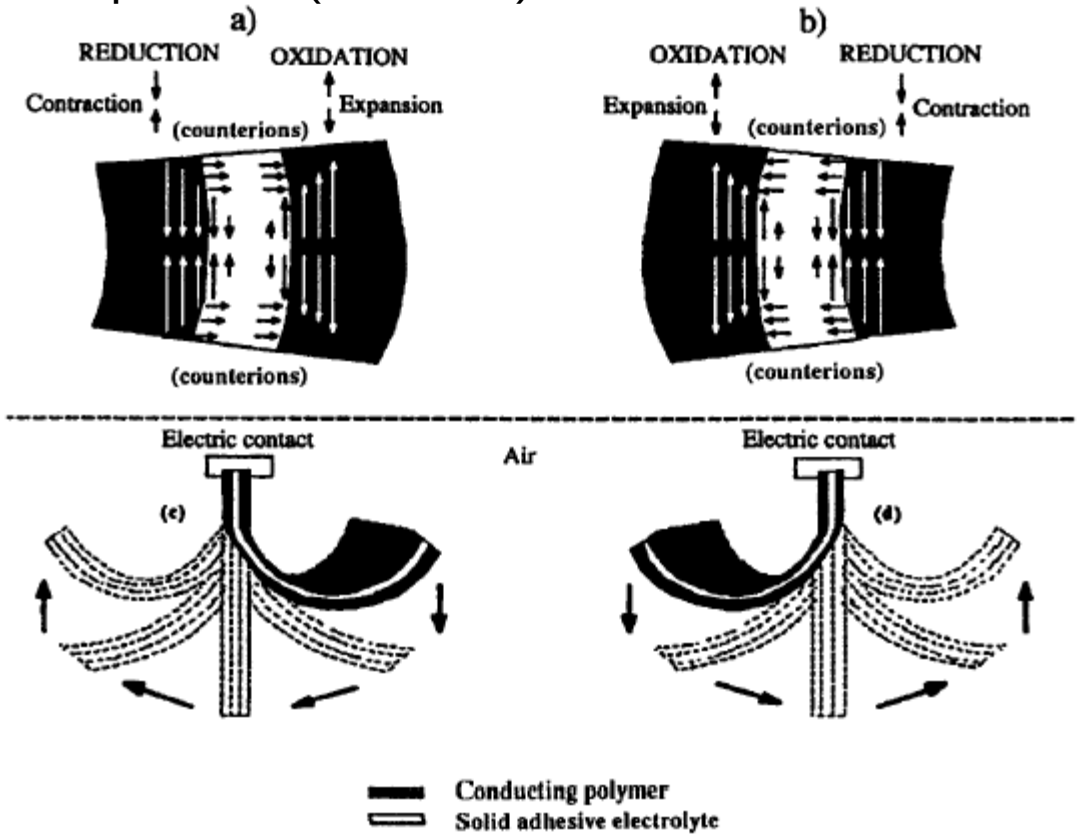
11. Biomimetic and bio-inspired materials

Smart polymers

Movement is triggered by applying a voltage.

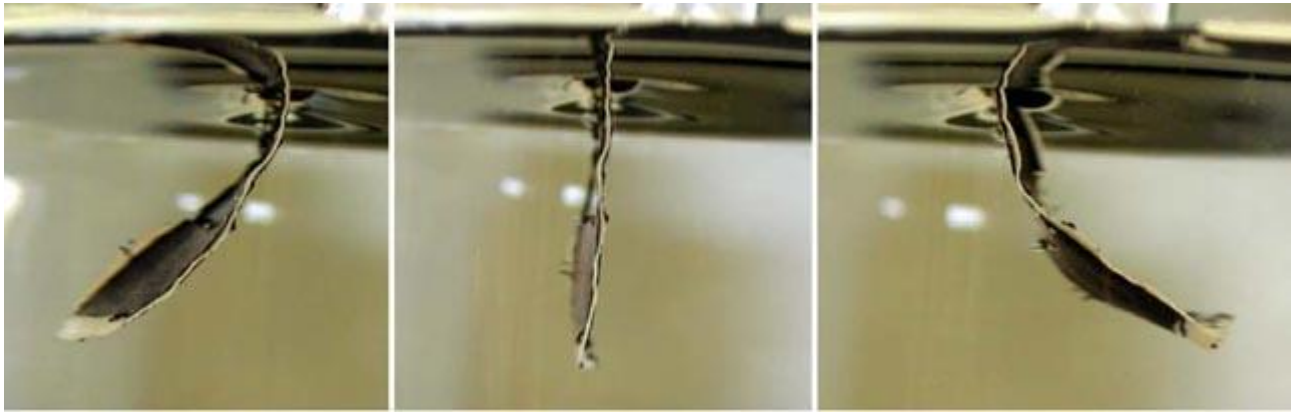
Electrochemically promoted transitions from neutral to oxidized state and back are accompanied by swelling and shrinking ant therefore trigger motion.

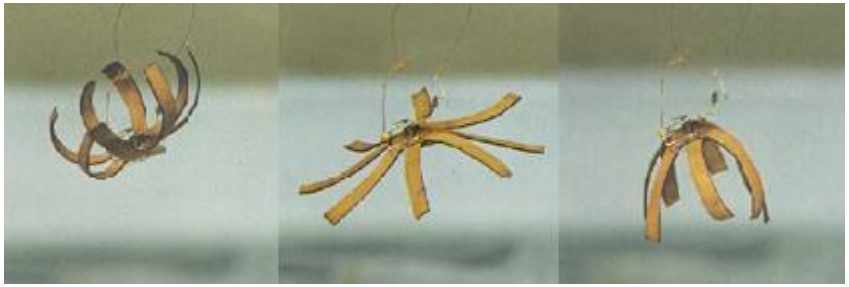
Small changes in potential (0.1-0.5 V) are sufficient.



11. Biomimetic and bio-inspired materials

Applications of smart polymers





Some Examples of Electroactive Polymers:

- Ionic Polymer Metal Composites (IPMCs)
- Conductive Polymers

http://eap.jpl.nasa.gov/

11. Biomimetic and bio-inspired materials

Summary

Imitating biological ***materials***:

- Bioduplication: artificial spider silk and resilin
- Bio-inspired: Velcro, lotus effect, moth eye

Imitating biological ***processes***:

- synthesis of nanoparticles
- bio-inspired mineralization
- motion: smart polymers

More about biomimetic materials and structures in:
892325, VO „Bionik - technische Lösungen aus der Natur“
H. Lichtenegger, BOKU, Institut für Physik und Materialwissenschaft
WS 2014/2015