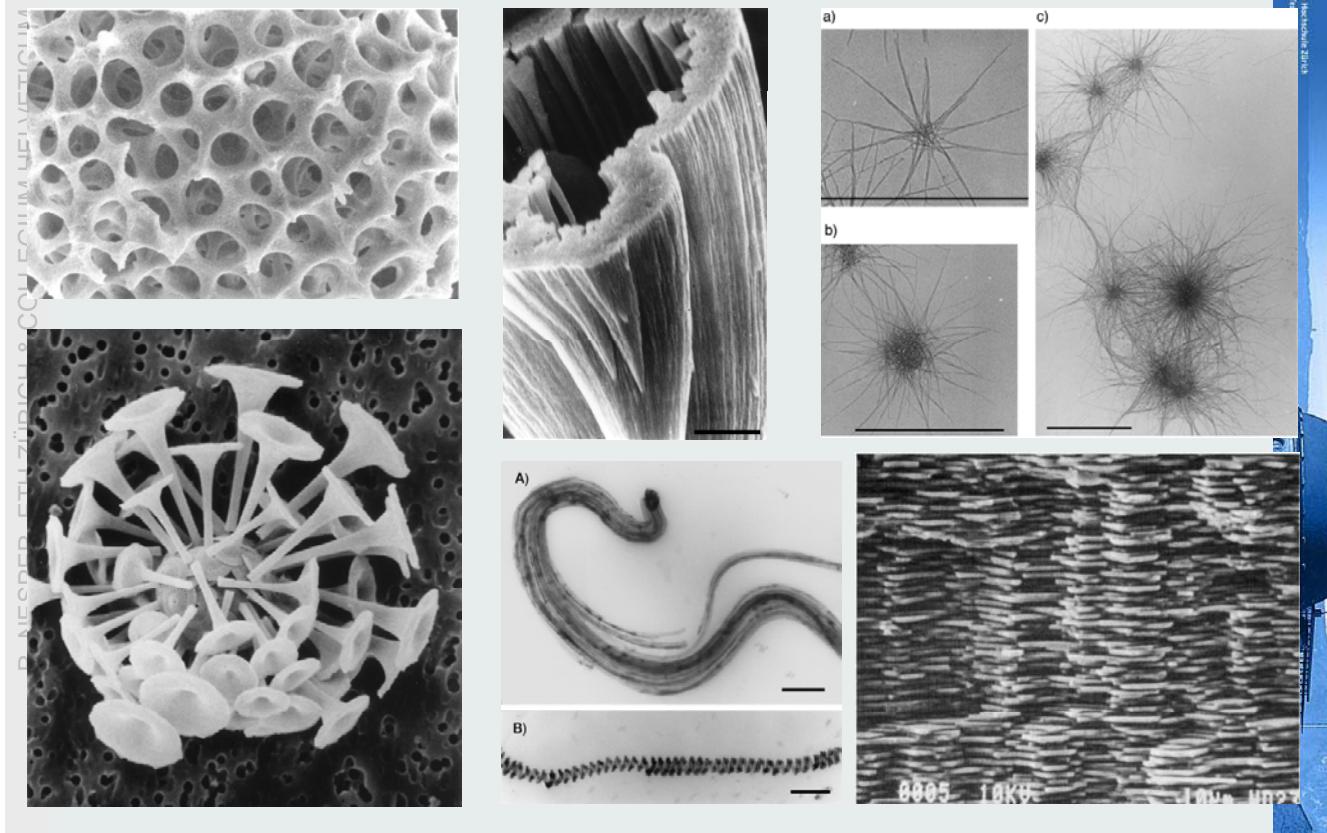


Forms of Minerals in Biology



Function of Minerals in Biology

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

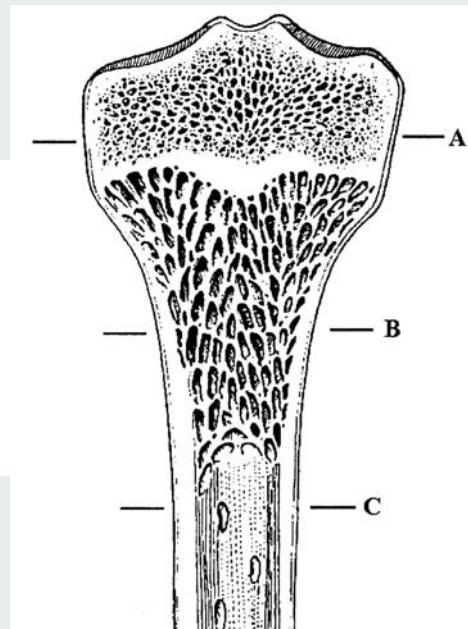


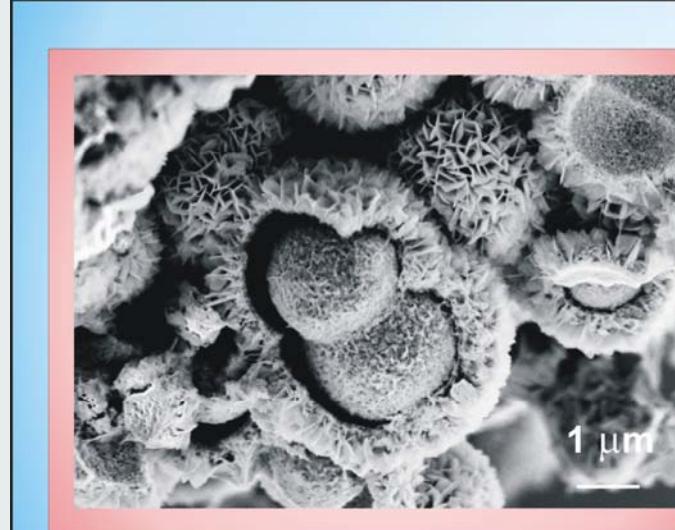
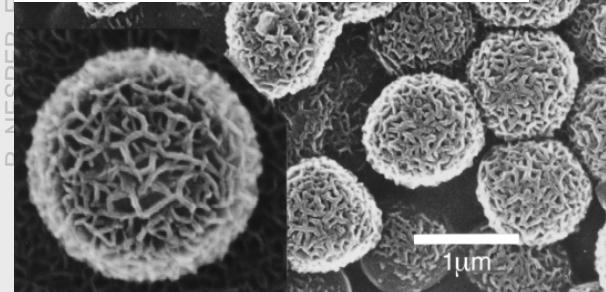
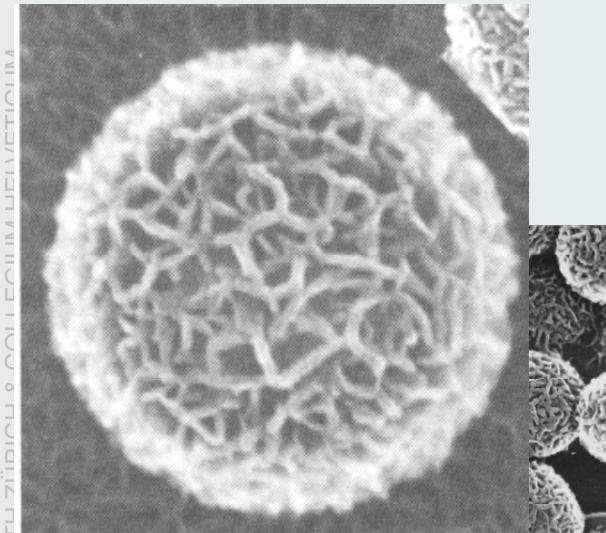
Fig. 2.9 Internal structure of long bone with three different microstructures (A, B and C).

Minerals in Biology

TABLE 11.8 Most Important Biominerals

Chemical Composition	Mineral Phase	Function and Examples
Calcium carbonate CaCO_3	Calcite Aragonite Vaterite Amorphous	Exoskeletons (e.g., egg shells, corals, mollusks, sponge spicules)
Calcium phosphates $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ $\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$ $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ $\text{Ca}_2(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$	Hydroxyapatite (HAP) Defect apatites Fluoroapatite Dicalcium phosphate dihydrate (DCPD)	Endoskeletons (bones and teeth)
$\text{Ca}_2(\text{HPO}_4)_2$	Dicalcium phosphate (DCPA)	
$\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$	Octacalcium phosphate (OCP)	
$\text{Ca}_3(\text{PO}_4)_2$	β -Tricalcium phosphate (TCP)	
Calcium oxalate $\text{Ca}_x\text{C}_2\text{O}_4 \cdot (1 \text{ or } 2)\text{H}_2\text{O}$	Whewellite Whedelite	Calcium storage and passive deposits in plants calculi of excretory tracts
Metal sulfates $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ SrSO_4 BaSO_4	Gypsum Celestite Baryte	Gravity sensors Exoskeletons (acantharia) Gravity sensors
Amorphous silica $\text{SiO}_n(\text{OH})_{4-2n}$	Amorphous (opal)	Defense in plants, diatom valves, sponge spicules, and radiolarian tests
Iron oxides Fe_3O_4	Magnetite	Chiton teeth, magnetic sensors
$\alpha, \gamma\text{-Fe(O)OH}$ $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	Goethite, lepidocrocite Ferrihydrite	Chiton teeth Chiton teeth, iron storage

Forms of Minerals in Biology



Reproducibility of Minerals in Biology

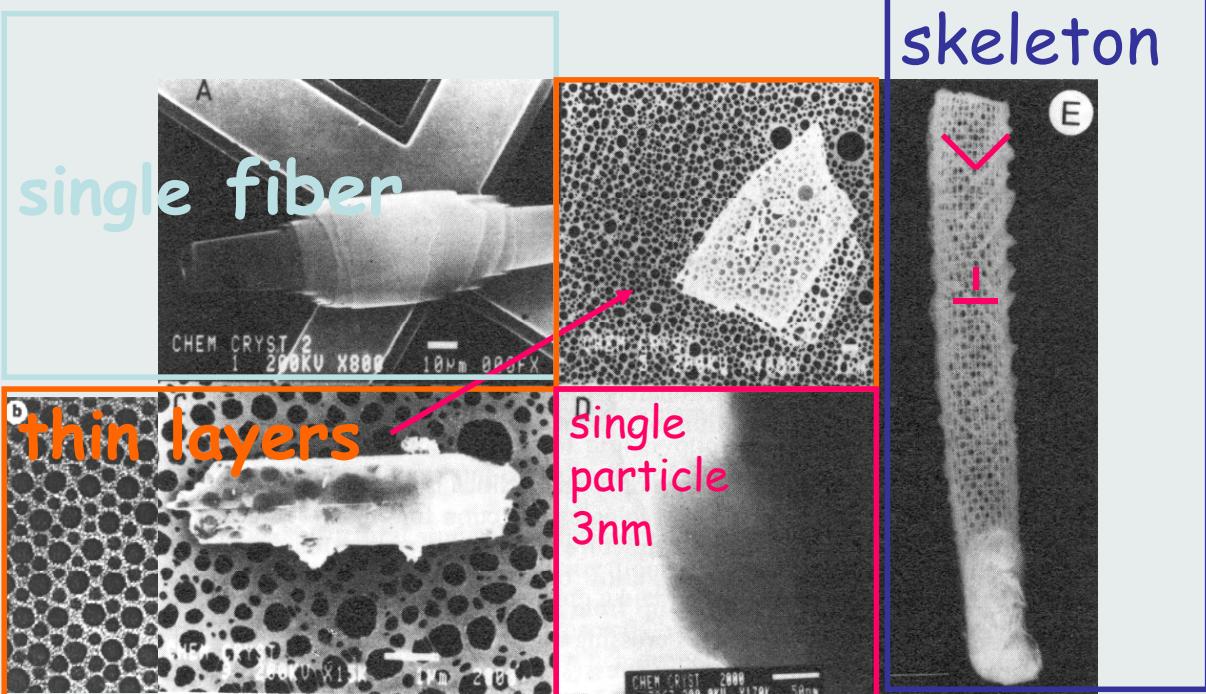
Table 2.3 Chemical composition of calcium phosphate (hydroxyapatite) in human and shark enamel

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

Nanochemistry UIO

5

Silica - deep sea sponge



C.C.Perry in S. Mann, J. Webb, R.J.P.Williams, Biominerization, VCH 1989

Nanochemistry UIO

Selfassembly

Spontaneous ordering of bimodal ensembles of nanoscopic gold clusters

C. J. Kiely*, J. Fink*†, M. Brust†, D. Bethell† & D. J. Schiffrin†
* Materials Science and Engineering, Department of Engineering,
The University of Liverpool, Liverpool L69 3BX, UK
† Department of Chemistry, The University of Liverpool, Liverpool L69 7ZD, UK

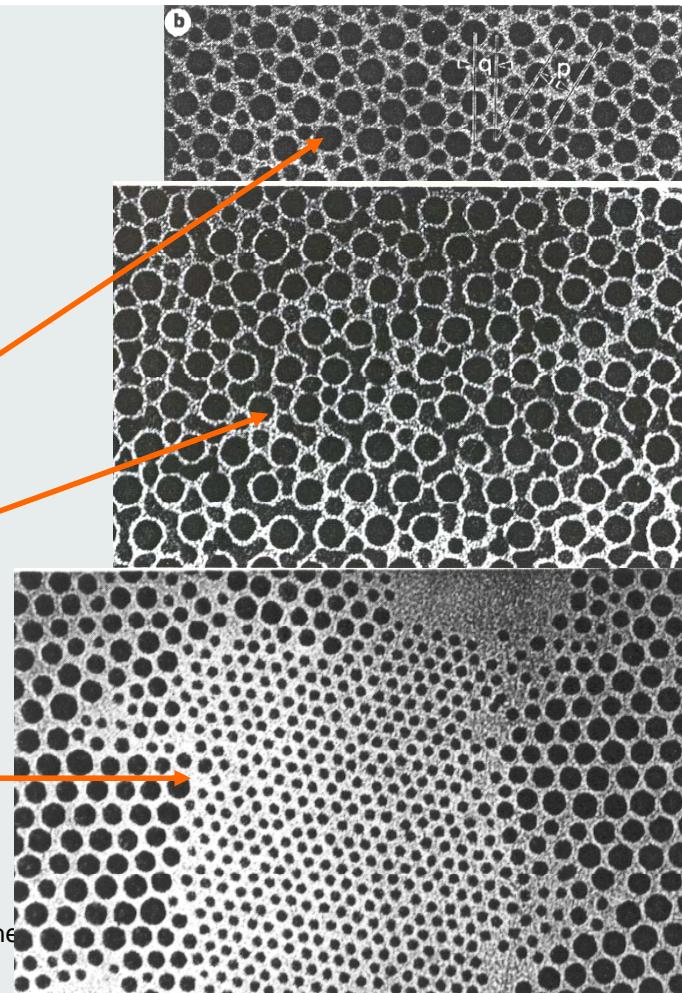
Nature (1998) 396, 444

primary structure

after aging

phase separation

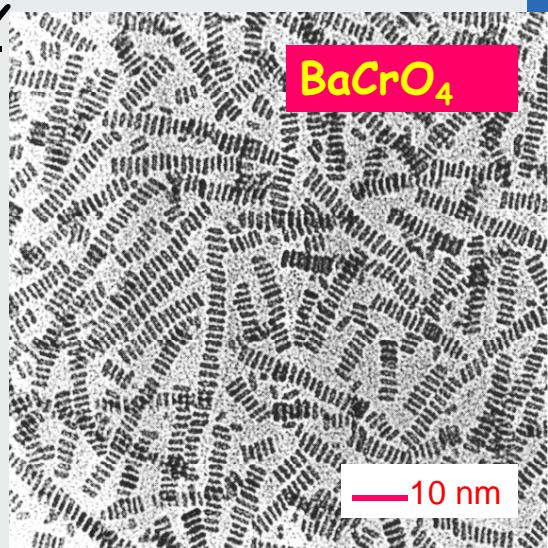
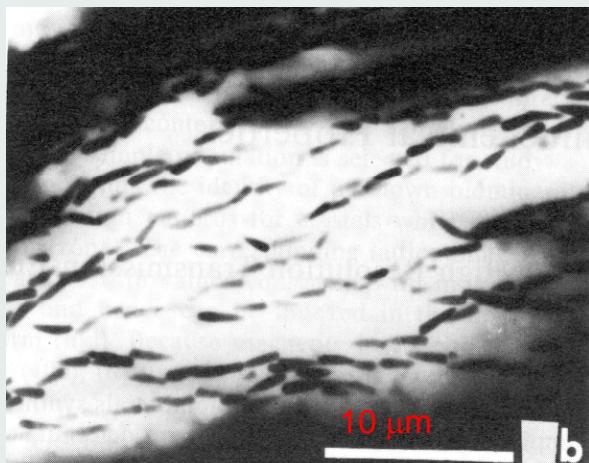
design - two cluster sizes



Advanced Selfassembly

Magnetosomes in algae

S. Mann, R.B. Frankel
in S. Mann, J. Webb,
R.J.P. Williams, Biominerization,
VCH 1989



Coupled synthesis and self-assembly of nanoparticles to give structures with controlled organization

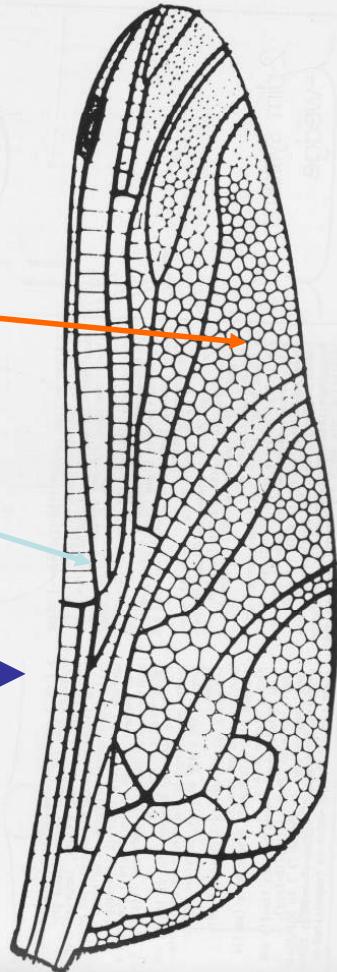
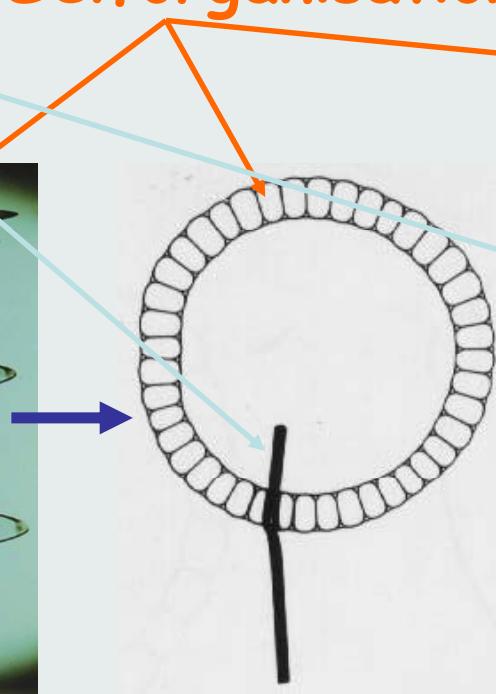
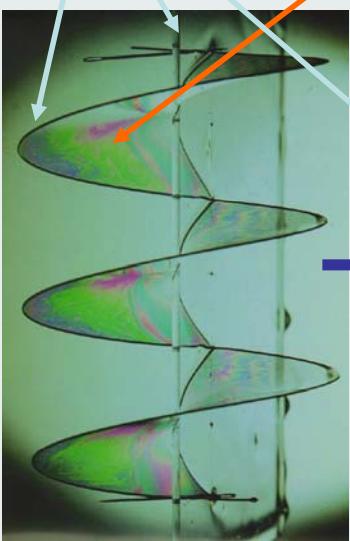
Mei Li*, Heimo Schnablegger† & Stephen Mann*

Nature (1999) 402, 393

Bio"mineralization"

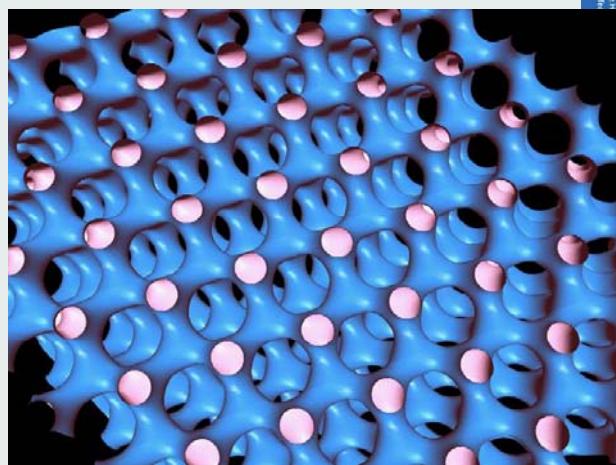
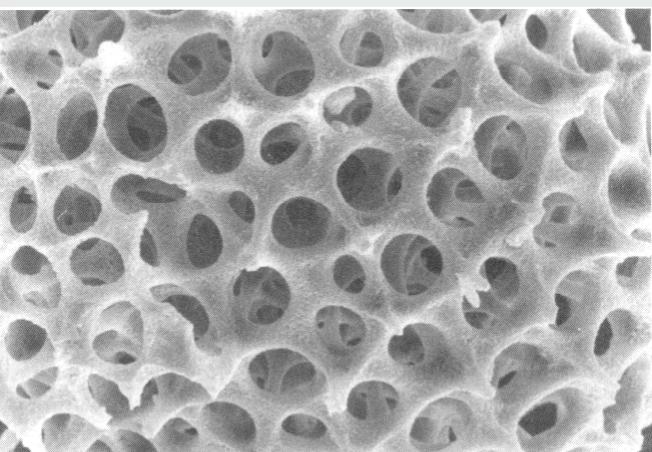
Design + Selforganisation

R. NESPER ETH ZÜRICH & COLLEGium HELVETICUM

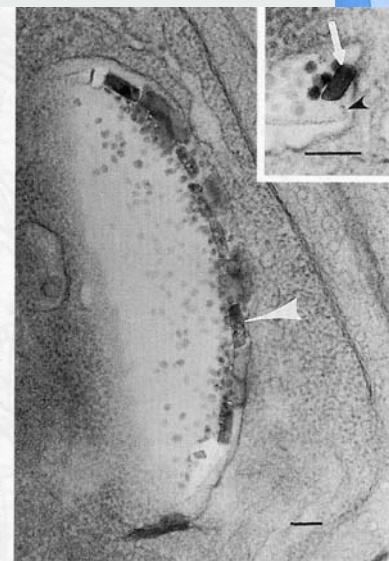
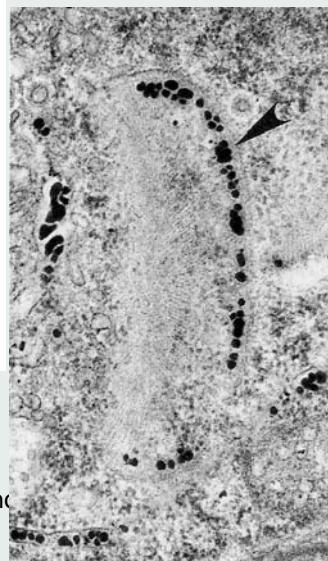
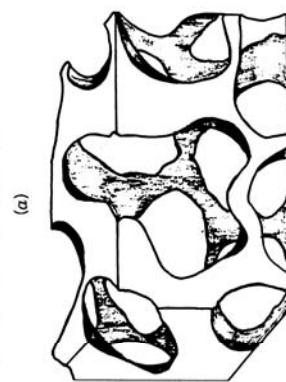
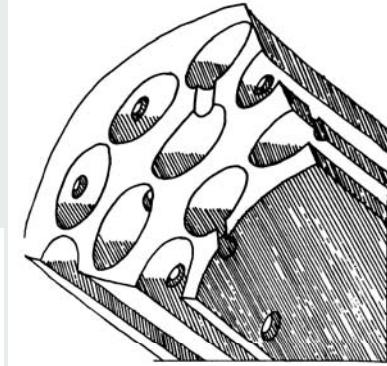
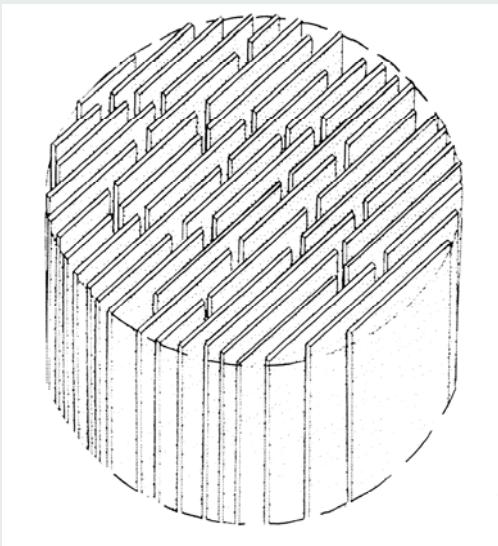


More Complex Forms of Minerals in Biology

R. NESPER ETH ZÜRICH & COLLEGium HELVETICUM



Design of Complex Forms



Nano

How is it achieved ?

Table 3.2 The main types of biominerization processes

Process	Control mechanism	Concepts	Properties	Chapter
Precipitation (crystallization)	Chemical	Solubility Supersaturation Nucleation Growth	Solution composition Promotion Inhibition Phase transformation	4
Boundary-organized biominerization	Spatial	Supramolecular preorganization	Physical boundary Diffusion-limited site Ion transport Size and shape Organization	5
Organic matrix-mediated biominerization	Structural	Interfacial molecular recognition	Site-directed nucleation Oriented nucleation Supporting framework Mechanical design	6
Morphogenesis	Morphological	Vectorial regulation	Complex form Time-dependent form Patterning	7
Biomineral tectonics	Constructional	Multilevel processing	Higher-order assembly Hierarchical structures Integrative building modules Adaptive structures and functions	8

What is achieved ?

- 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.

What is achieved ?

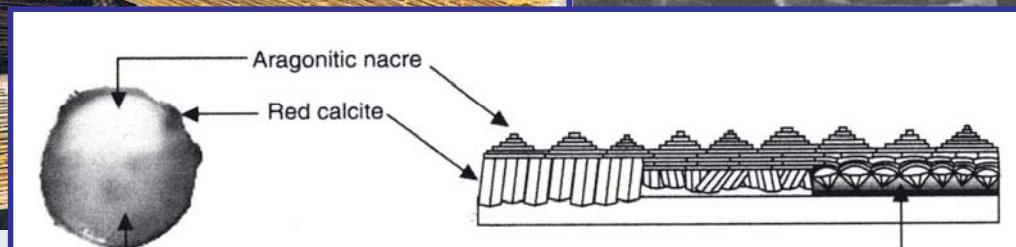
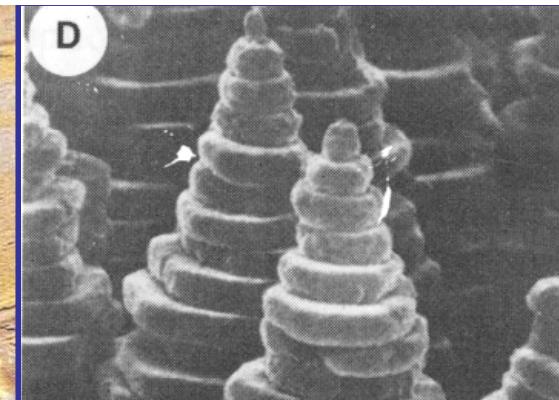
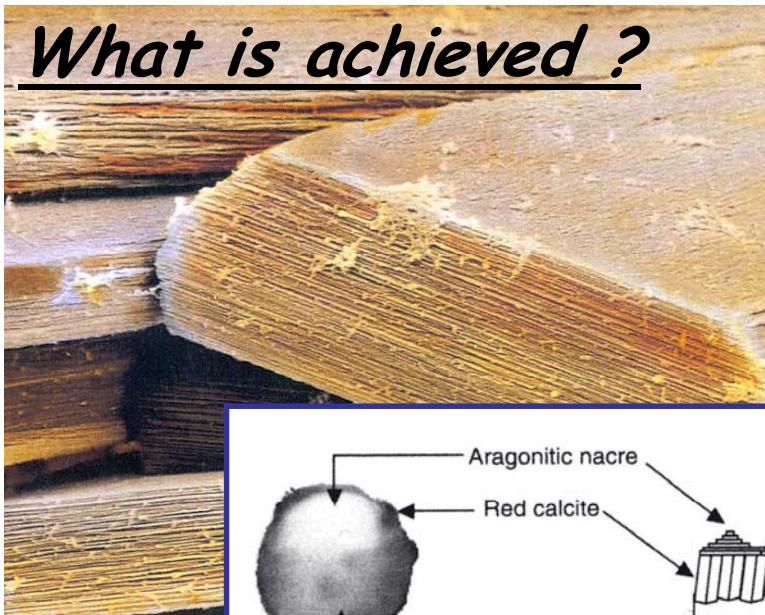


Figure 15.3 A mature flat pearl. The c-axis of the nacre is perpendicular to the paper. The three different regions of the flat pearl are labeled red calcite, aragonitic nacre and green organic layer. The schematic diagram on the right shows the spatial organization of the regions.

Toughness

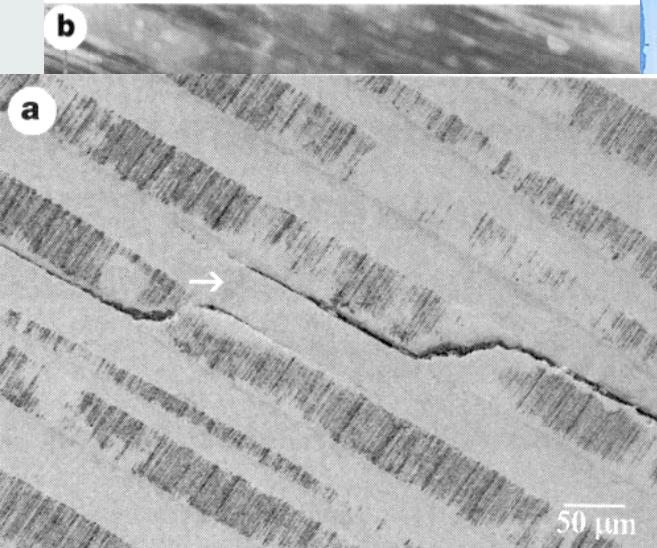
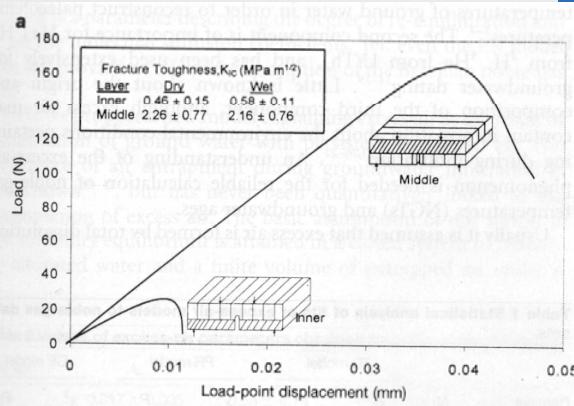
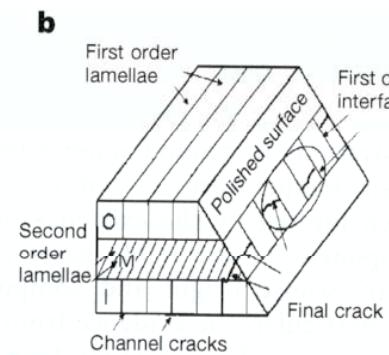
Structural basis for the fracture toughness of the shell of the conch *Strombus gigas*

S. Kamat*, X. Su*, R. Ballarini† & A. H. Heuer*

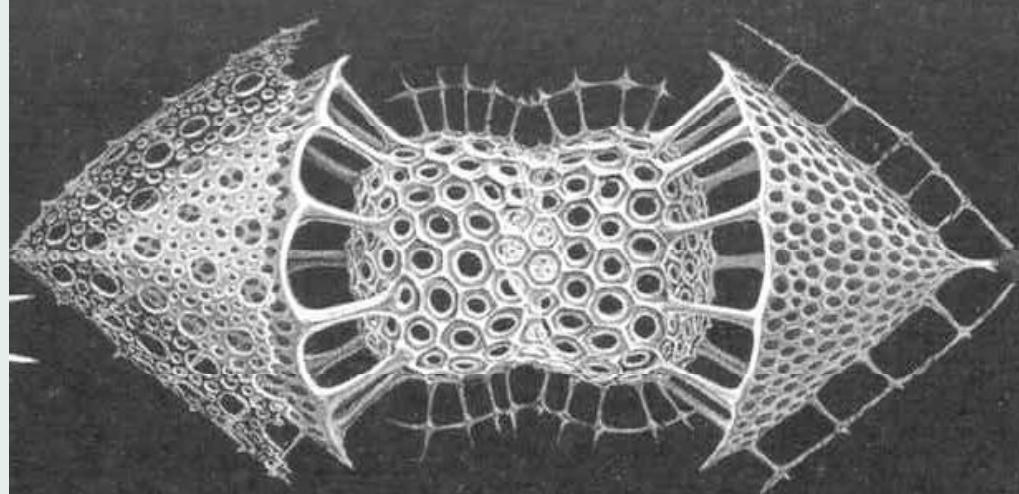
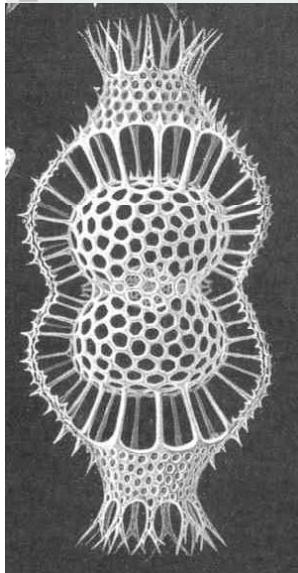
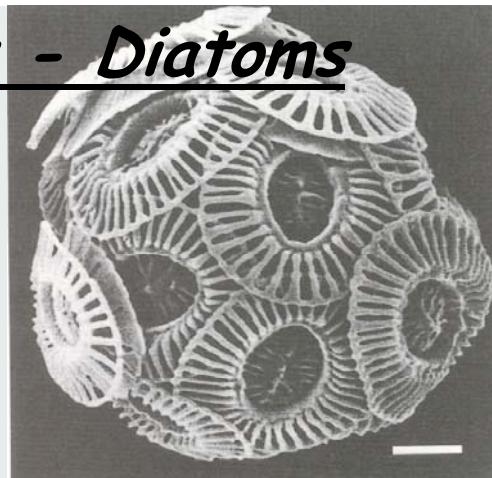
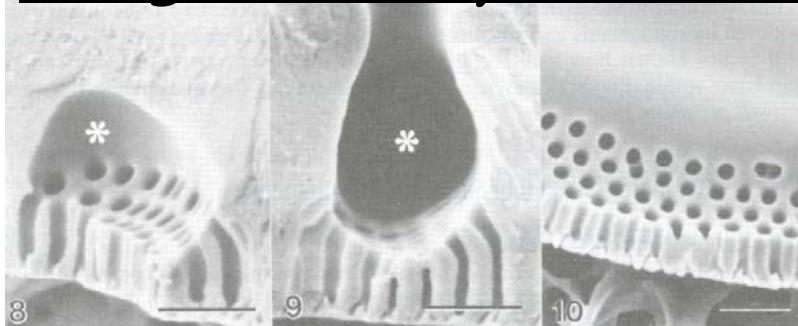
Nature 405 (2000) 1038

ZÜRICH & COLLEGIAL

- Layers : 0.5-2mm
1. Order lamella : 5-60mm
2. Order lamella : 5-30mm
3. Order lamella : 60-130nm



Design of Complex Forms - Diatoms



How is it achieved ?

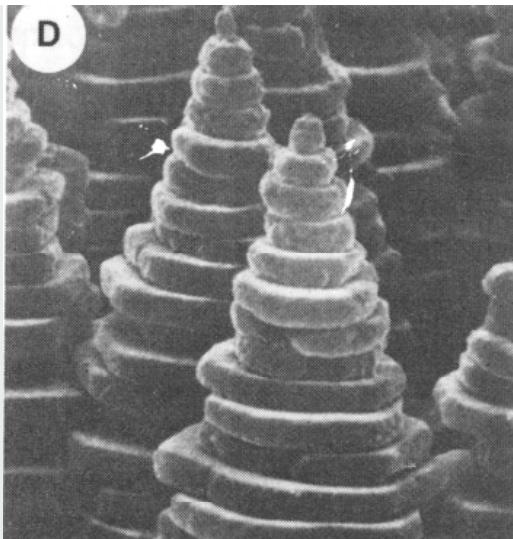
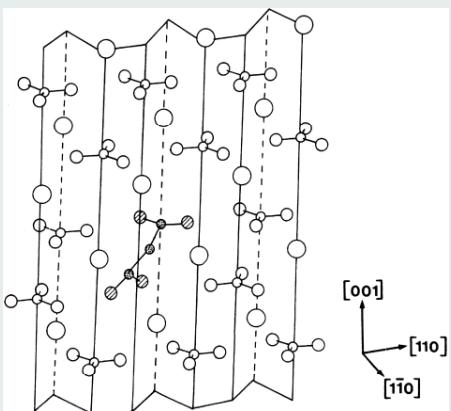
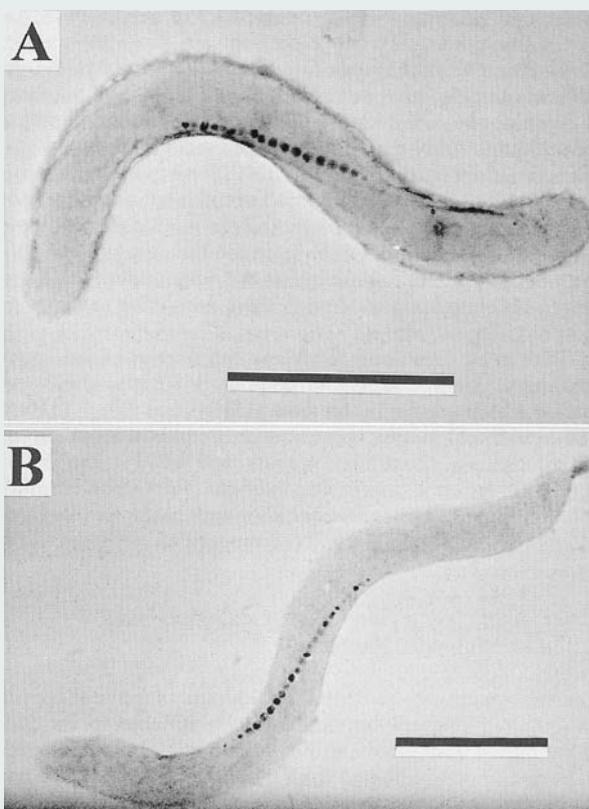


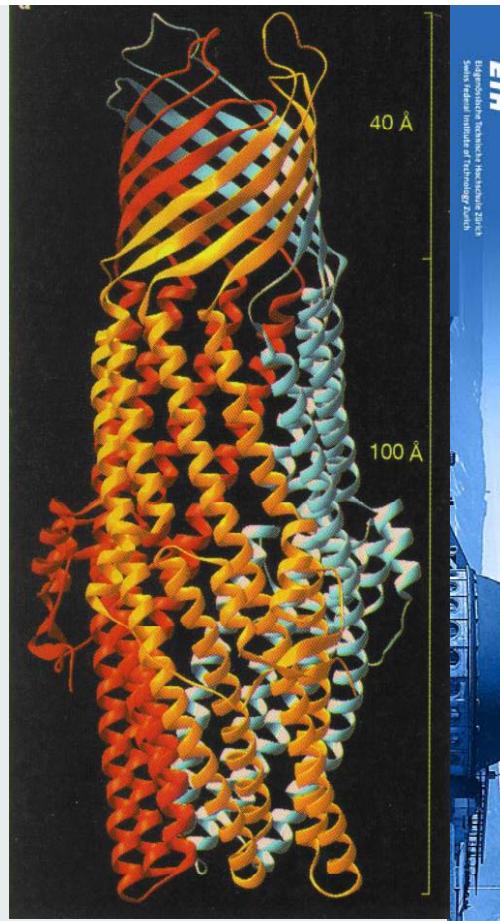
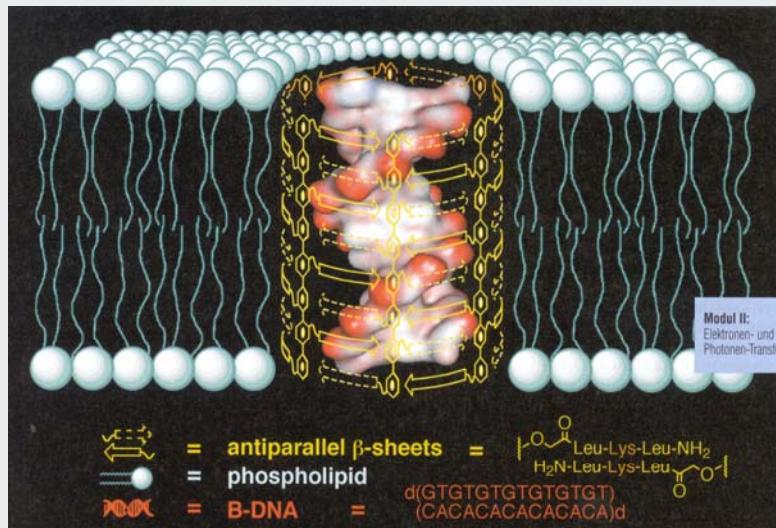
Fig. 4.23 Computer model showing side view of the calcite $\{1\bar{1}0\}$ face with surface-bound polyaspartate ($[Asp]_{11}$).

Control and Function

- chemical
- spatial
- structural
- morphological
- constructional.



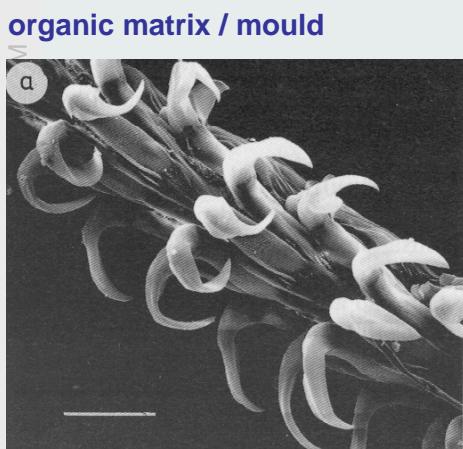
Control and Function



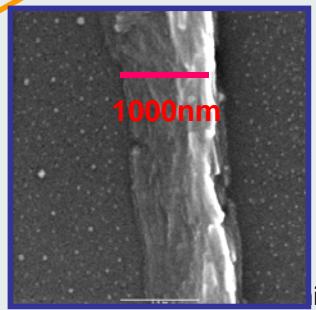
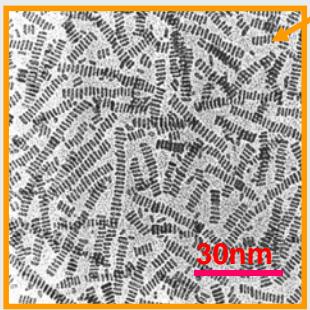
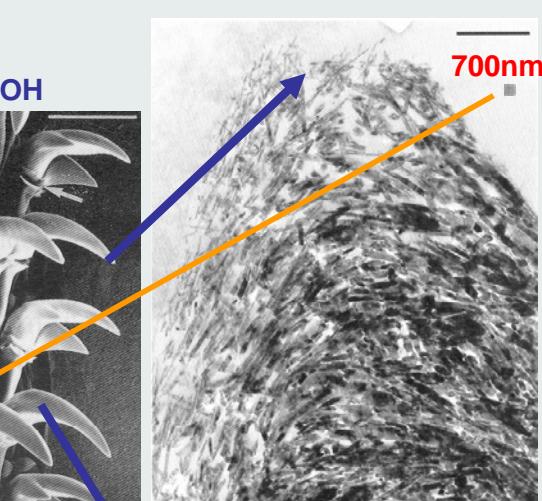
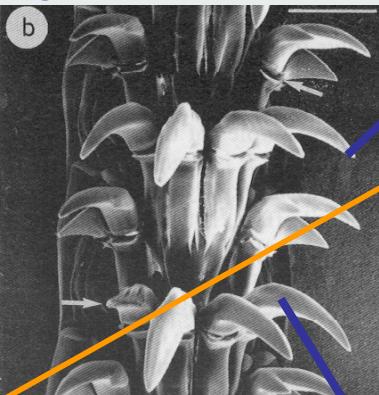
Nanochemistry UIO

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Structural Alignment



Composite
organic + α -FeOOH



J. Webb, D.J. Macey, S. Mann
in S. Mann, J. Webb, R.J.P. Williams,
Biominerization, VCH 1989

Biodynamic Restoration

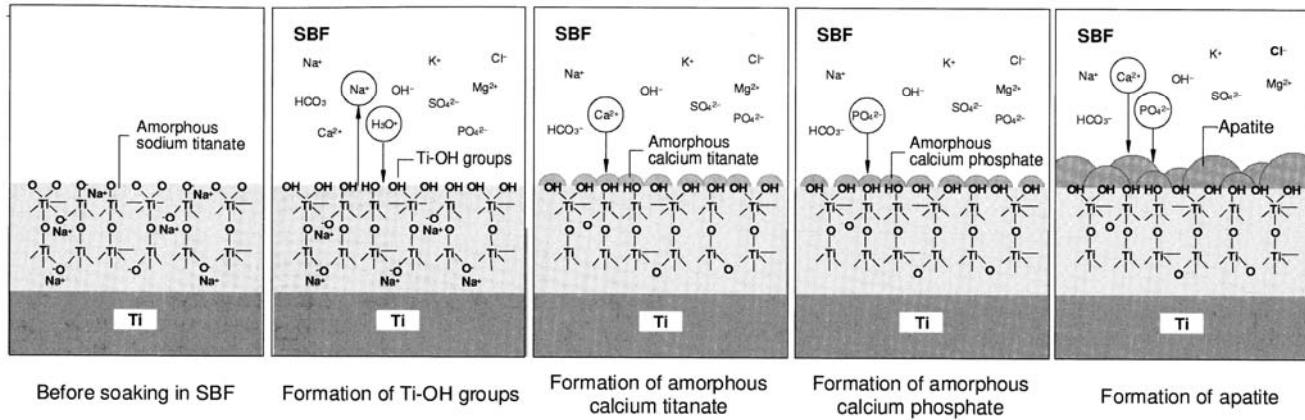


Figure 2. Schematic representation of the mechanism of apatite formation on NaOH-treated Ti metal in simulated body fluid (SBF) (from Reference 10).

Enamel Formation

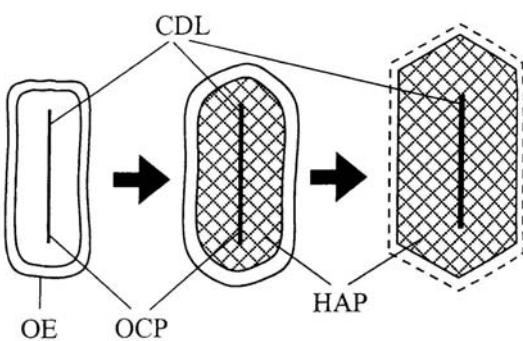


Fig. 4.30 Formation of enamel crystals. An octacalcium phosphate (OCP) precursor phase is formed within an organic envelope (OE) and then overgrown with a single crystal of hydroxyapatite (HAP). Traces of the OCP phase are left as a central dark line (CDL) inside the mature crystal.

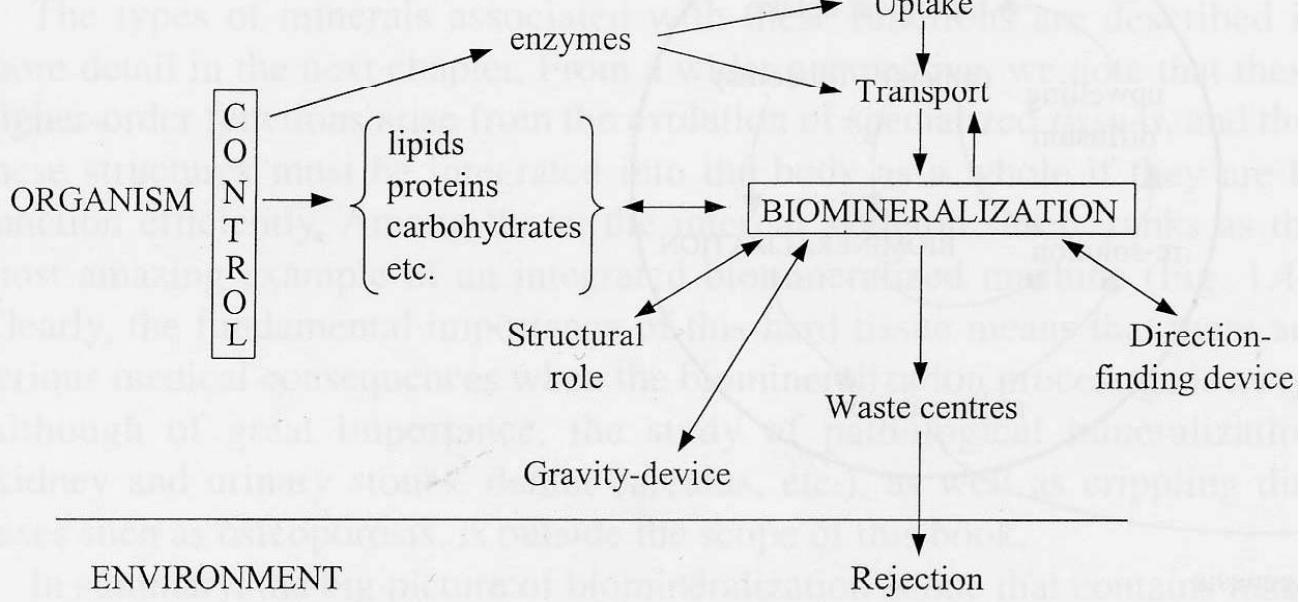
Table 4.2 Epitaxial deposition of inorganic crystals on inorganic substrates. A positive percentage misfit value indicates that the overgrowth lattice is larger than the substrate lattice

Substrate	Overgrowth	Lattice misfit %
PbS	Nal	8
	KCl	5
	NaBr	-1
	NaCl	-6
	AgBr	-4
	AgCl	-7
	RbBr	7
	RbCl	3
	KBr	3
	Nal	1
CaCO ₃	KCl	-2
	NaBr	-7
	NaBr	8
	NaCl	3
	LiBr	0
CaF ₂	LiCl	-6
	NaBr	6
	NaCN	6
	AgBr	3
	AgCN	3
NaCl	AgCl	1
	KF	-5

Living System

ENVIRONMENT

Abundance and Availability



Nanochemistry UIO

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Living System

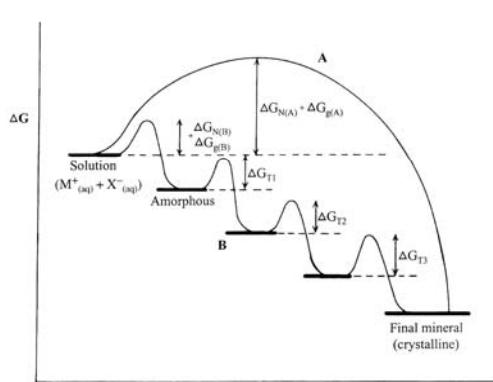
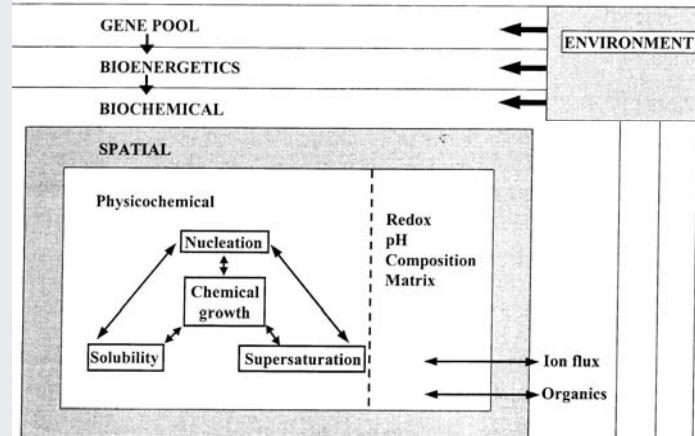


Fig. 4.25 Pathways to crystallization and polymorph selectivity: (A) direct (B) sequential. See text for details.

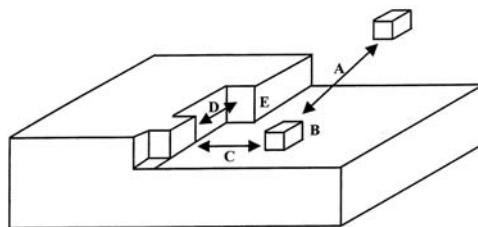


Fig. 4.6 Layer-by-layer mechanism of crystal growth. See text for details.

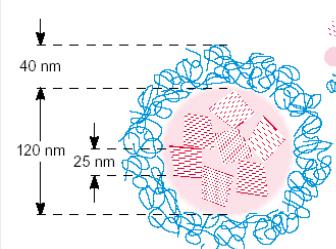
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Biosensors



Tumor + Gene Therapy



β-Carotin-Aggregate
amorphes β-Carotin
Schutzkolloid

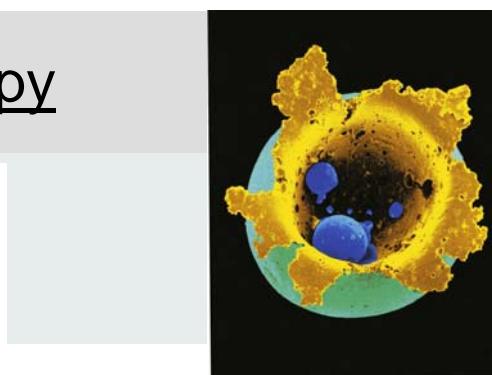


Abbildung 27. Kern-Schale-Aufbau der β-Carotin-Hydrosol-Partikel. Den spektroskopischen Daten und den Weitwinkelröntgenspektren (WAXS) zufolge besteht der Wirkstoff-Kern aus H- und J-Aggregaten mit Abmessungen bis zu 30 nm, entsprechend einer maximalen Aggregationzahl von 10000 Molekülen.

