Bioapatites

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Mineralized („hard”) tissues:

- Bones
- Teeth
  - Enamel
  - Cementum
  - Dentin

- Hydroxy(l)-apatite

Composition of hard tissues:

	Enamel	Dentine	Cementum	Bone
Total inorganic	97	70	61	65
Total organic	1.5	20	27	25
Water	1.5	10	12	10
Ash:				
Calcium*	36.5	35.1	35.2	34.8
Phosphorus*	17.7	16.9	16.1	15.2
Ca/P ratio	1.63	1.61	1.71	1.71
Sodium*	0.5	0.6		0.9
Magnesium*	0.44	1.23	0.73	0.72
Potassium*	0.08	0.05		0.03
Fluoride*	0.01	0.06	<0.05	0.03
Cloride*	0.3	0.01		0.13
Unashed (dry tissue):				
Carbonate	3.5	5.6	5.5	7.4
Pyrophosphate	0.022	0.1		0.07

Data correspond to 100 g dry weight.

Composition of enamel, dentin and cementum:

- Enamel:
  - 96-99% anorganic substances
  - 1-2% organic substances
    - NO collagen!
    - Mature enamel: enamelin and TRAP (tyrosin rich protein)
    - Immature enamel: enamelin and amelogenin
  - 3% water
  - density: 3 mg/ml

See: Mineralized tissues practice!!!

Composition of enamel, dentin and cementum:

- Dentin:
  - 70% anorganic substances
  - 20% organic substances
    - Collagen is the major protein
    - Polyanions
      - Sulfated acidic glycoproteins
      - Phosphoproteins
  - 10% water
  - density: 2.1 mg/ml

See: Mineralized tissues practice!!!

Composition of enamel, dentin and cementum:

- Cementum:
  - 61% anorganic substances
  - 27% organic substances
    - Collagen is the major protein
    - Polyanions
      - Sulfated acidic glycoproteins
      - Phosphoproteins
  - 12% water
  - density: approx. 2.1 mg/ml

See: Mineralized tissues practice!!!

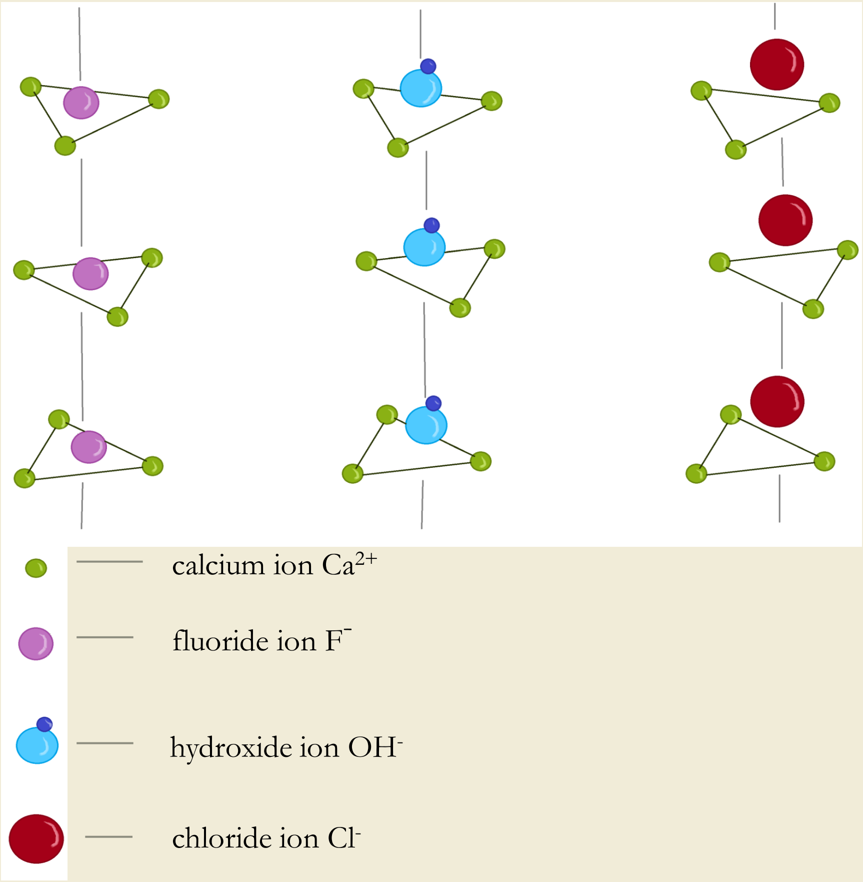
Composition of enamel, dentin and cementum:

- Water
  - Free water
  - Bound water to organic molecule
  - Water built in crystal strucure
- Organic substances
  - Organic components with nucleator function:
    - Polyanions – chelate binding with Ca ions
  - Matrix proteins
    - Collagen, enamelin, amelogenin
  - Regulatory proteins

See: Mineralized tissues practice!!!

Ionic radius of incorporated ions into apatite crystals

Substituents	Ionic radius (Å)
Cations:	
Ca^{2+}	0.99
Sr^{2+}	1.12
Pb^{2+}	1.2
Ba^{2+}	1.33
Anions:	
OH^{-}	1.53
F^{-}	1.36
Cl^{-}	1.81



Types of calcium phosphates:

- Ortho- (PO_4^{3-})
- Pyro- ($P_2O_7^{4-}$)
- Poly- ($(PO_3)_n^{n-}$)

  phosphates

- Apatite-substituents
  - Fluorapatite, chlorapatite
- Dahllites
  - Poorly crystallized forms of hydroxyapatites

Types of calcium phosphates:

Name	Formula	Abbreviation	Ca/P ratio	Occurence
brushite - dicalcium phosphate dihydrate	$CaHPO_4*2H_2O$	DCPD	1.0	pathological calcifications: calculus, crystalluria, chondrocalcinosis, urinary stones
monetite – dicalcium phosphate anhydrate	$CaHPO_4$	DCPA	1.0	calcium-phosphate cement, nutritional supplements, tabletting aids, toothpaste components
octacalcium phosphate	$Ca_8(HPO_4)_2(PO_4)_4*5H_2O$	OCP	1.33	Dental and urinary calculi
whitlockite	$Ca_9(Mg,Fe)(PO_4)_6(HPO_4)$	WH	1.41	dental calculus, dentine caries, urinary stones
β-tricalcium phosphate	$\beta\text{-}Ca_3(PO_4)_2$	β-TCP	1.5	
amorphus calcium phosphate	$Ca_x(PO_4)_y*nH_2O$	ACP	1.2-2.2	calcification sites, mitochondria
hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	HA	1.67	bone, enamel, dentine, calculus

FEATURES OF CRYSTALLIZATION

General regularities:

- The Gibbs-Kelvin principle:
  - Standard free energy ↑
  - Entropy ↓
- Optimum: the particles are as close as possible to one another → maximal volume filling
  - Ionic radius
  - Charge of the components
- **Dynamic balance!** – enamel surface – hydroxy(l)-apatite (*de- and remineralization*)

General regularities:

- Supersaturated solution → crystal formation
- At several points, they are merging → **cluster formation** →
  - Relative surface area ↓
  - Dissolution ↓

  } → Crystal growth

  - Impurity ions
  - **Fault location**

  } → Crystal stabilty deteriorates

    - **Missing lattice point**
    - **Increased distance between two lattice points**

Homogeneous and heterogeneous nucleation:

- Homogeneous nucleation:
  - Only inorganic components of the crystal
  - High energy is required
- Heterogeneous nucleation:
  - Nuclei forming organic substances – polyanions
    - » (see: above)
  - Less energy is required → more favorable for living organisms → typical crystallization method of hard tissues
  - Matrix proteins – binding Ca-chelates
    - Collagen, amelogenin

Homogeneous and heterogeneous nucleation:

- Homogeneous nucleation:
  - Seeding: preformed crystals are put in a saturated solution
    - To start the crystallization process
  - Seeding (nuclei formation):

    can occur *in vivo* – primery enamel formation

    » (see: Dentinogenesis and Amelogenesis lectures)
  - Epitaxy: two crystals grow on each other – two types crystal structures!
  - Mononuclear – layer by layer growing
  - Polynuclear – highly supersaturated solution or

    - multiple nuclei

Factors influencing crystallization:

- Quality of calcium phosphates
  - Well/poorly crystallized Ca-P-s
  - Size
  - Stability
  - Speed

  Differencies (Size, Stability, Speed)
- Rate of supersaturation
- Temperature
  - Dissolution - solidification
- pH
- Nucleation

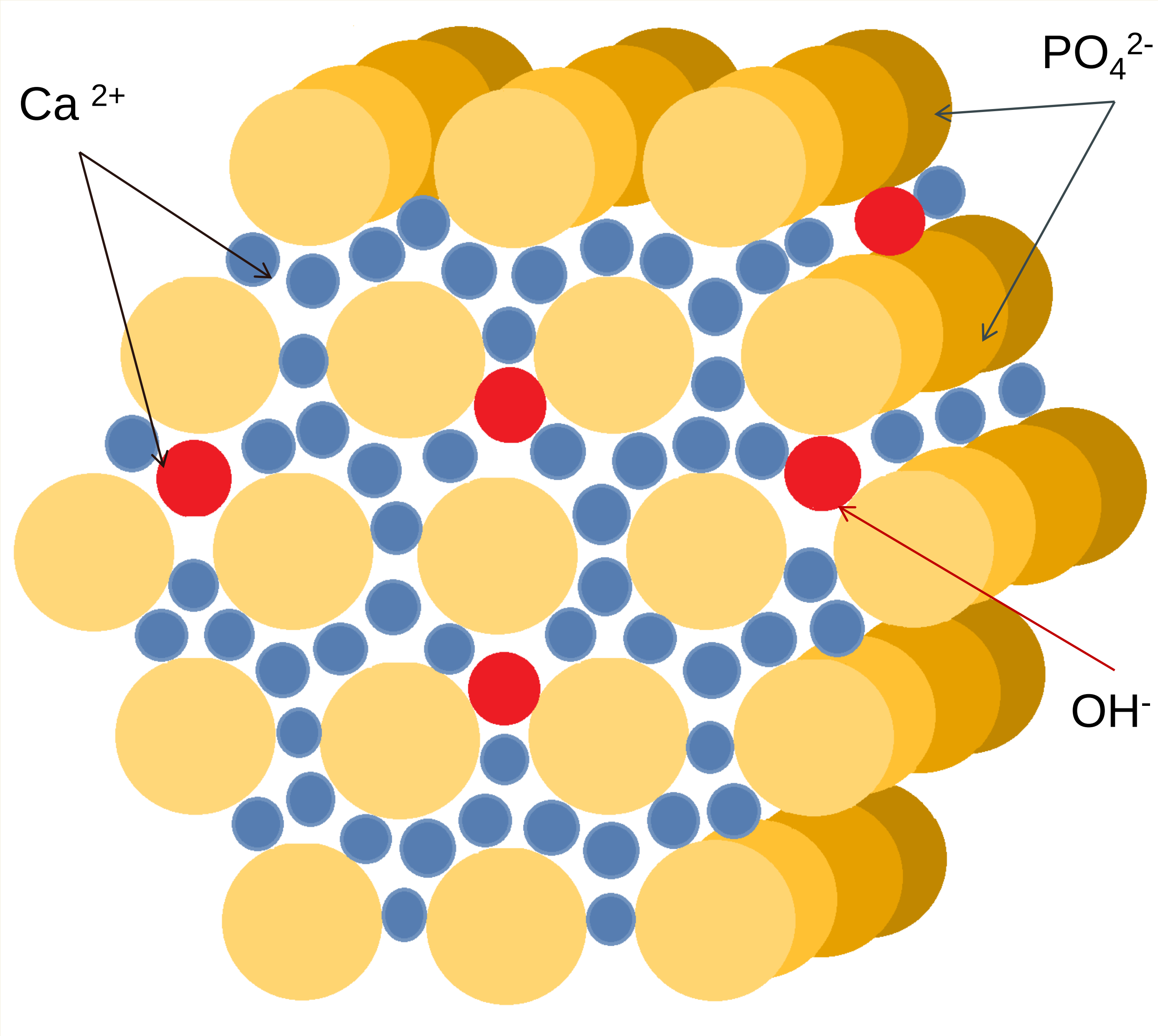
  » (see: above)

Factors influencing crystallization:

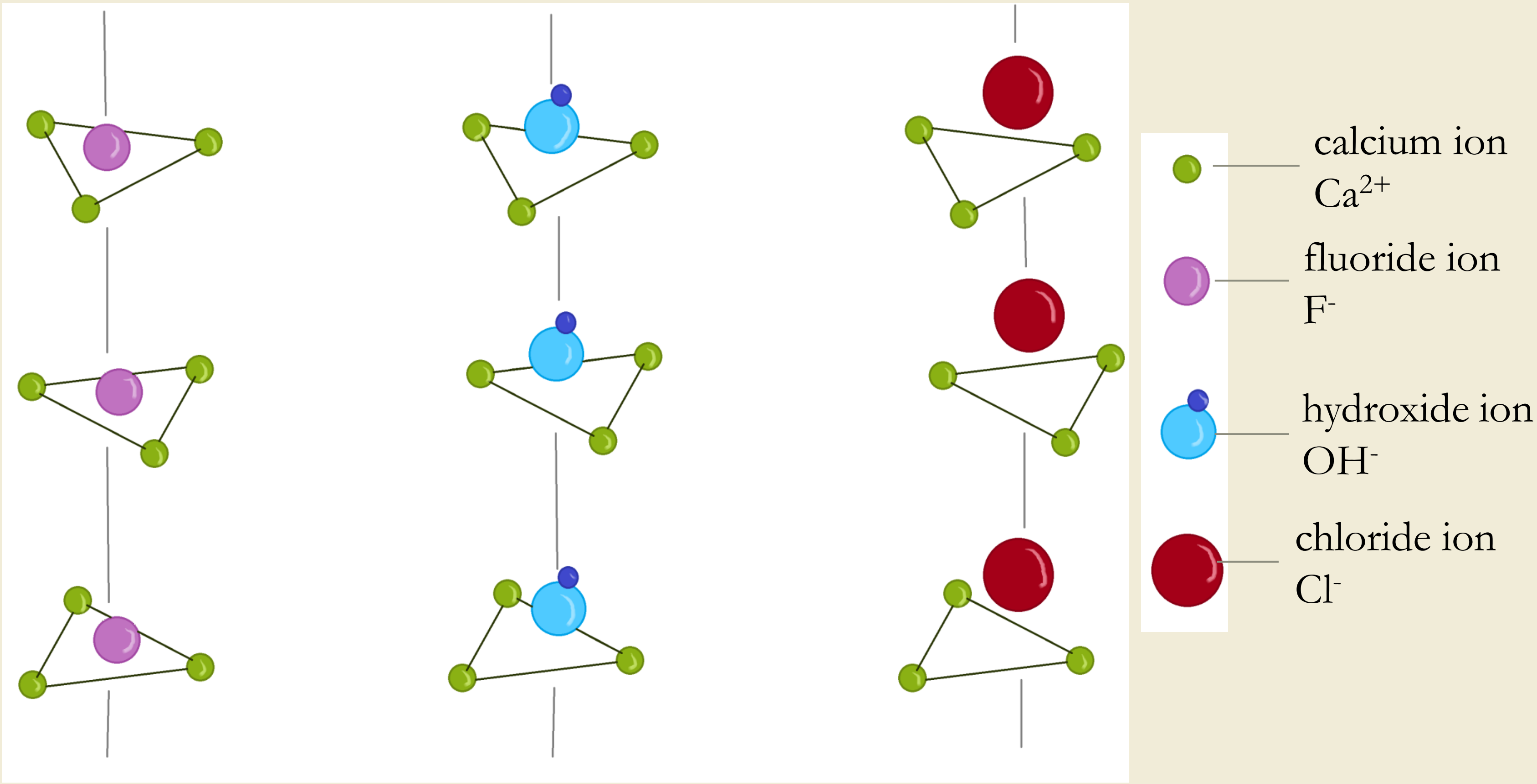
- Matrix proteins
  - » (see: above)
- Trace elements
  - » (see: later)
- Inhibitors
  - – Mg, ADP inhibit the crystallization in mitochondria
- Substances reacting with Ca or P-s

SPATIAL STRUCTURE OF APATITE CRYSTALS

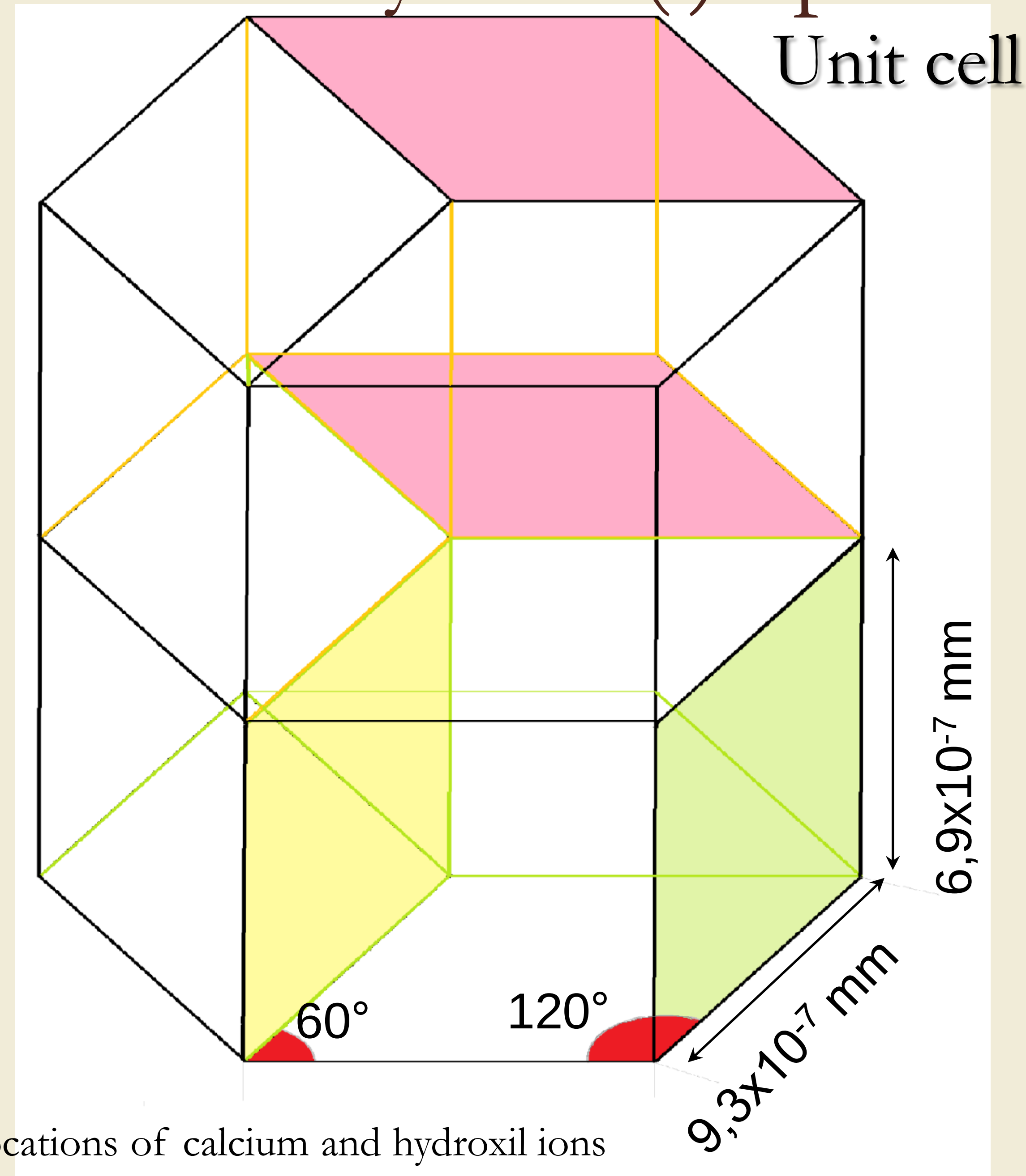
Structure of hydroxi(l) apatite



Structure of hydroxi(l) apatite



Stucture of hydroxi(l) apatite



Spatial locations of calcium and hydroxil ions

Structure of hydroxi(l) apatite

- Enamel, dentin – hexagonal prisms
- Size of enamel prisms > dentin prisms
  - Amount of heterogenous nucleator is less in enamel crystal
  - Enamel becomes more dense
    - Loses – organic material
    - - and water content

- Amorphus-CaP – not crystallized
- Brushite – plate-like crystals

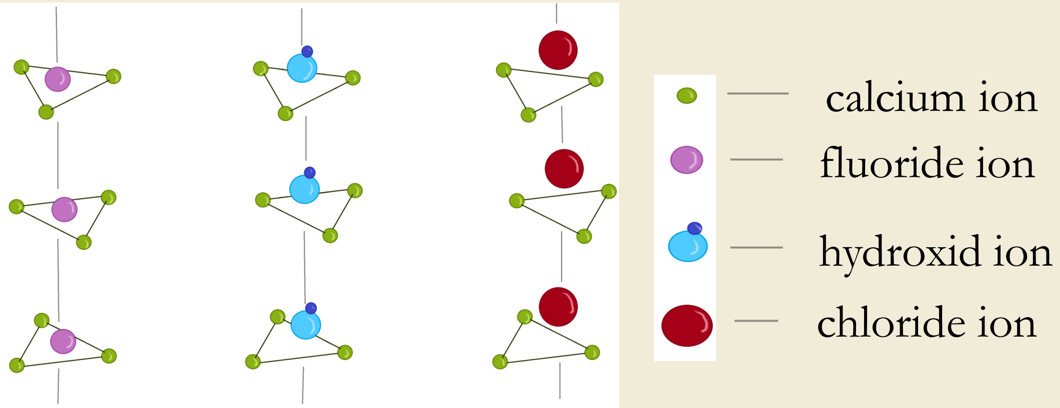
Trace elements effects on apatite crystals:

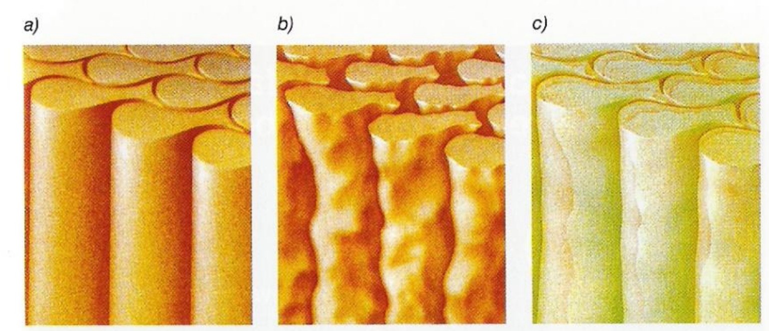
- Cariogenic trace elements:
  - Al – exerts its effects through binding to the crystal surface
  - Hg, Cd, Pb
  - Cu, Se

- Carioprotective trace elements:
  - F, Sn, Sr – incorporated into the crystal
  - Mo, V

Advantages of fluorapatites:

- ***Effect on enamel hydroxil apaptite:***
  - Reducing the acid solubility
  - Strengthening the crystal structure
  - Remineralisation of demineralised areas
- ***Effect on enamel surface:***
  - Inhibitions of proteins and/or bacteria adsorption
  - Reducing the surface energy





8.3. ábra. A zománc struktúrája állandóan változik: *(a)* ép zománcprizmák, *(b)* demineralizálódott zománcprizmák, *(c)* remineralizálódott zománcprizmák