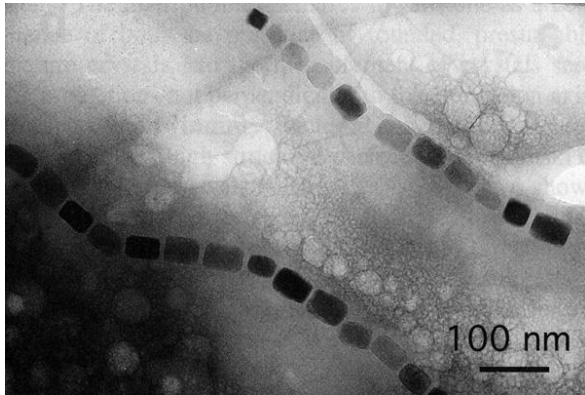


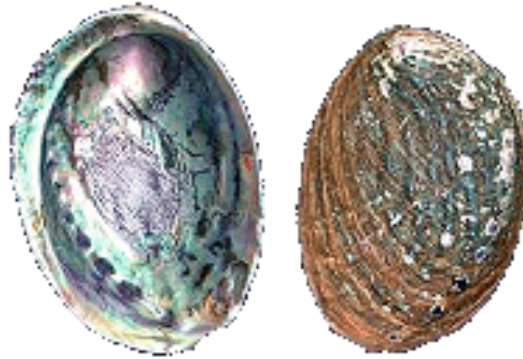
Analytical techniques applied to biominerals characterization



Alejandro B. Rodríguez-Navarro
Departamento de Mineralogía y Petrología
UNIVERSIDAD DE GRANADA



Bacterial magnetosomes



Haliotis shell



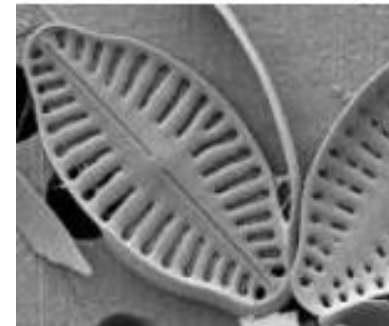
Corals



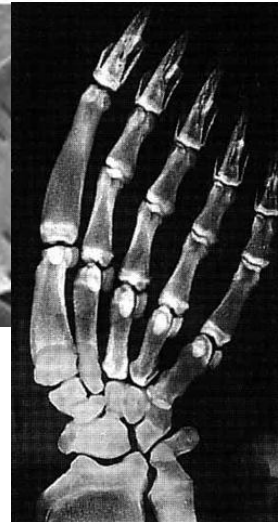
coccoliths



Hen eggshell

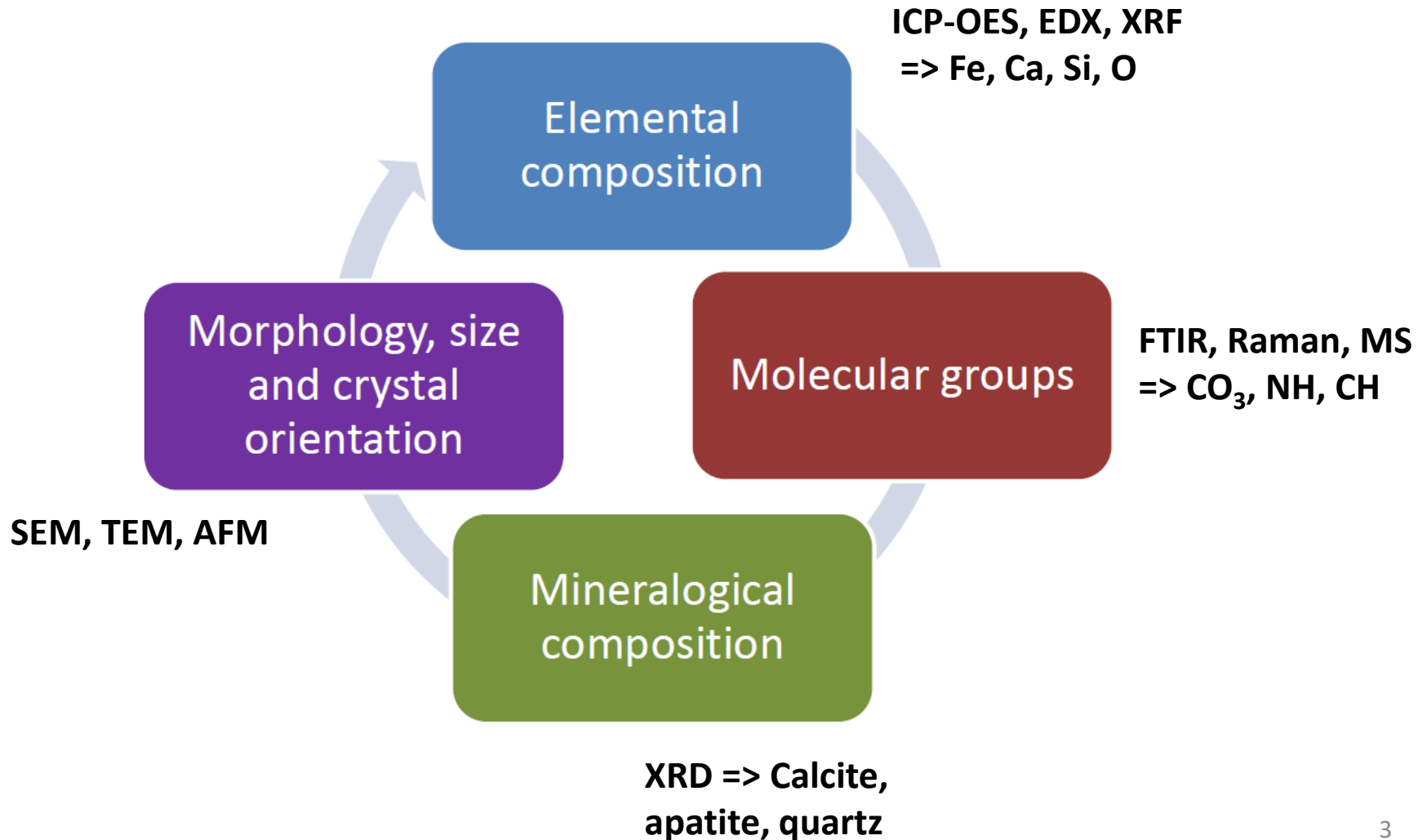


Diatomeas

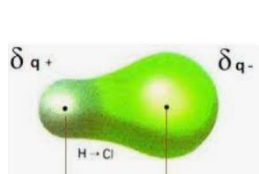
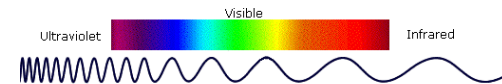


Human bone

Analytical techniques

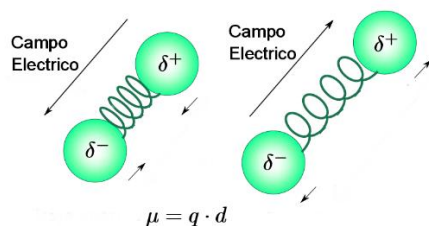


Infrared spectroscopy



$$\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}}$$

Dipolar moment > 0 IR active



Hooke's law

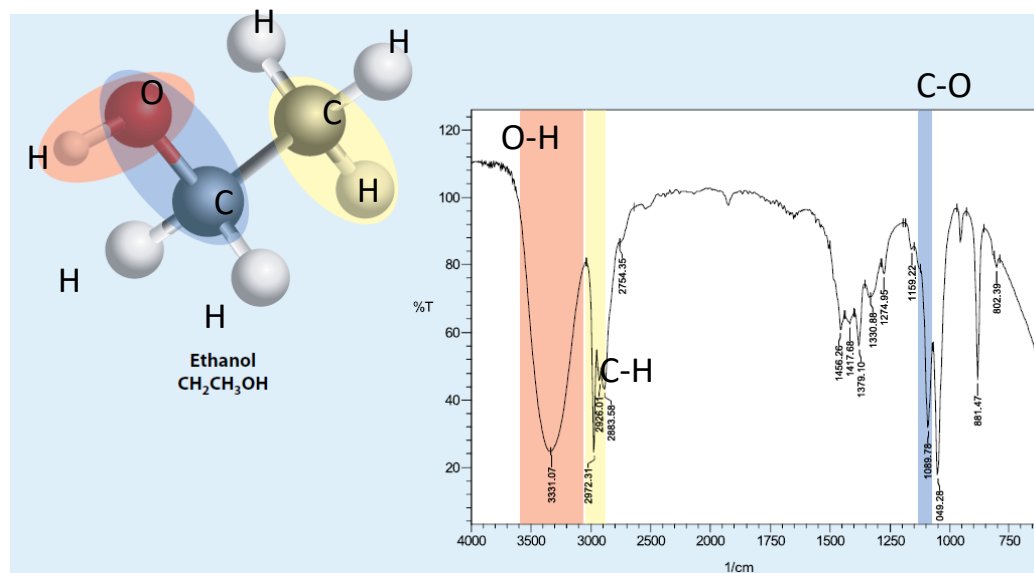
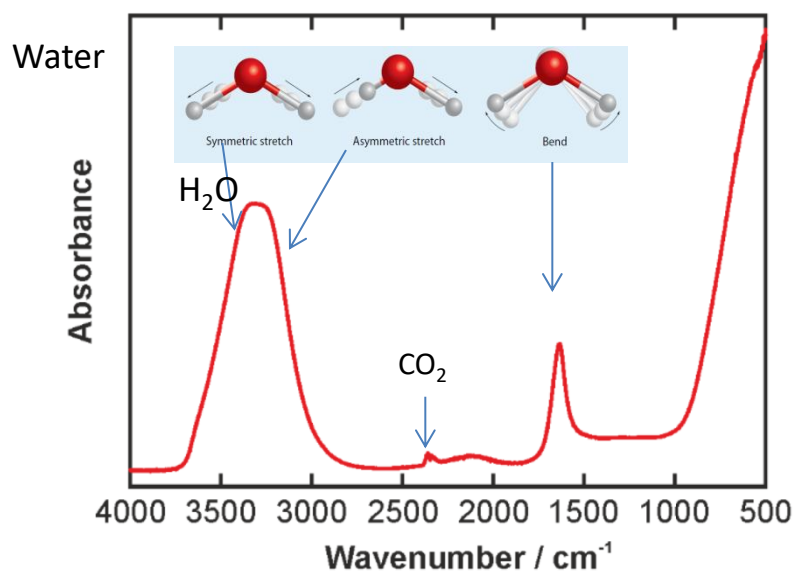
$$\tilde{\nu} = k \sqrt{\frac{f}{m}}$$

stronger bond $\rightarrow$ higher frequency

f = force constant
 m = mass
 k = constant

smaller mass $\rightarrow$ higher frequency

Each molecular bond: C-H (lipids), C-O (carbonates), P-O (phosphates), C-N (proteins), C-O-C (polysaccharides) vibrates at specific frequencies.



Measuring IR spectra (FTIR)



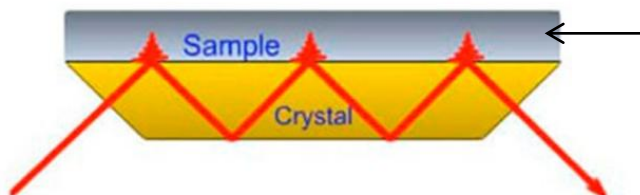
Transmission: KBr disc



Espectrometro FTIR
Jasco



Reflection: ATR (diamond, SeZn, Ge crystal)

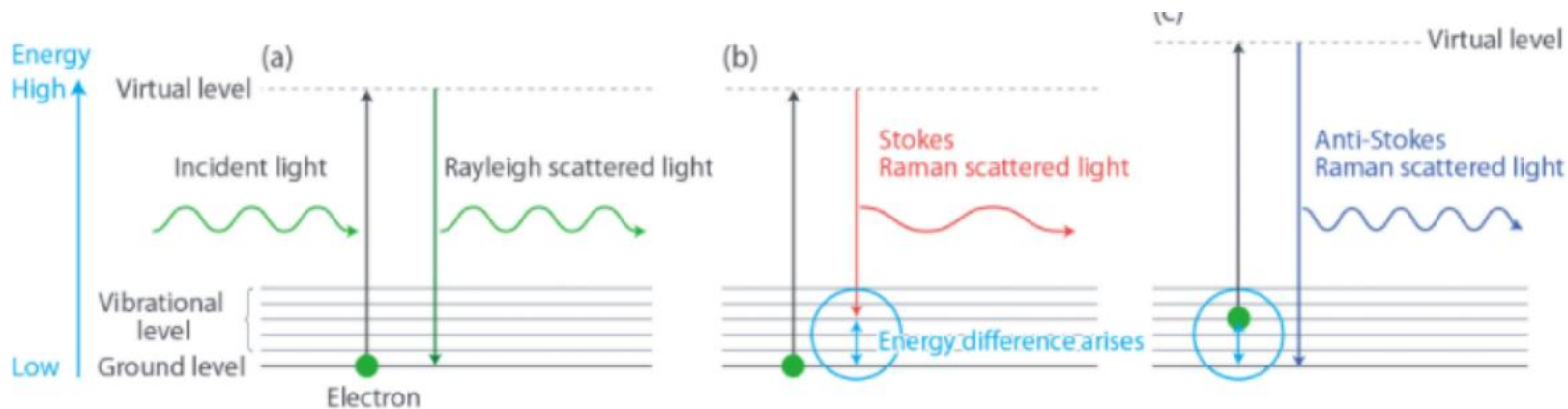


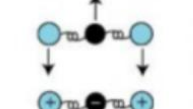
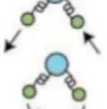
Evanescent wave
< 2 μm (diamond, Ge)

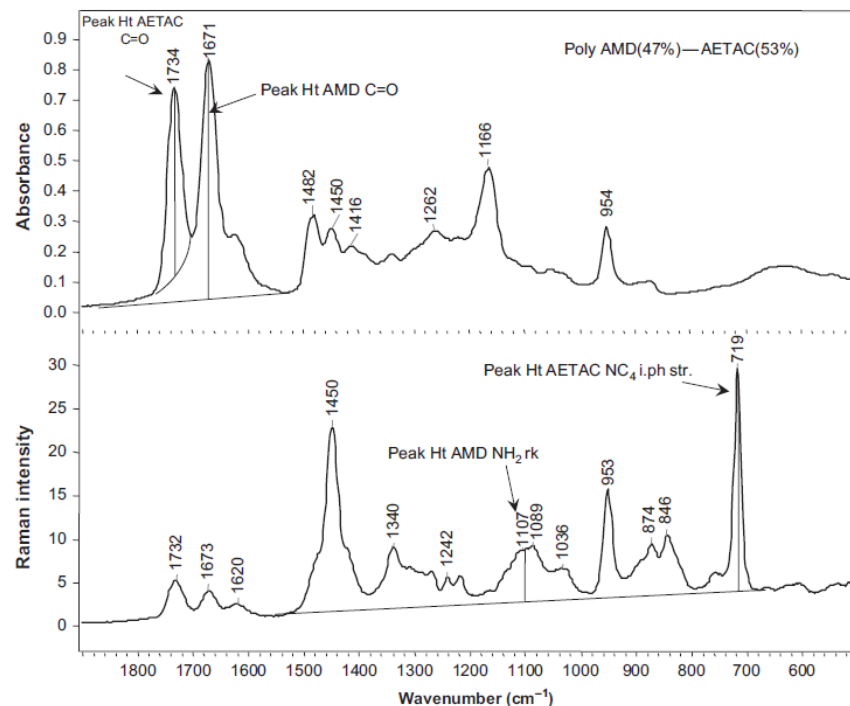
Surface analysis

Spectroscopía RAMAN

Inelastic or Raman scattering, monochromatic light, LASER, molecular bonds. Complementary to IR

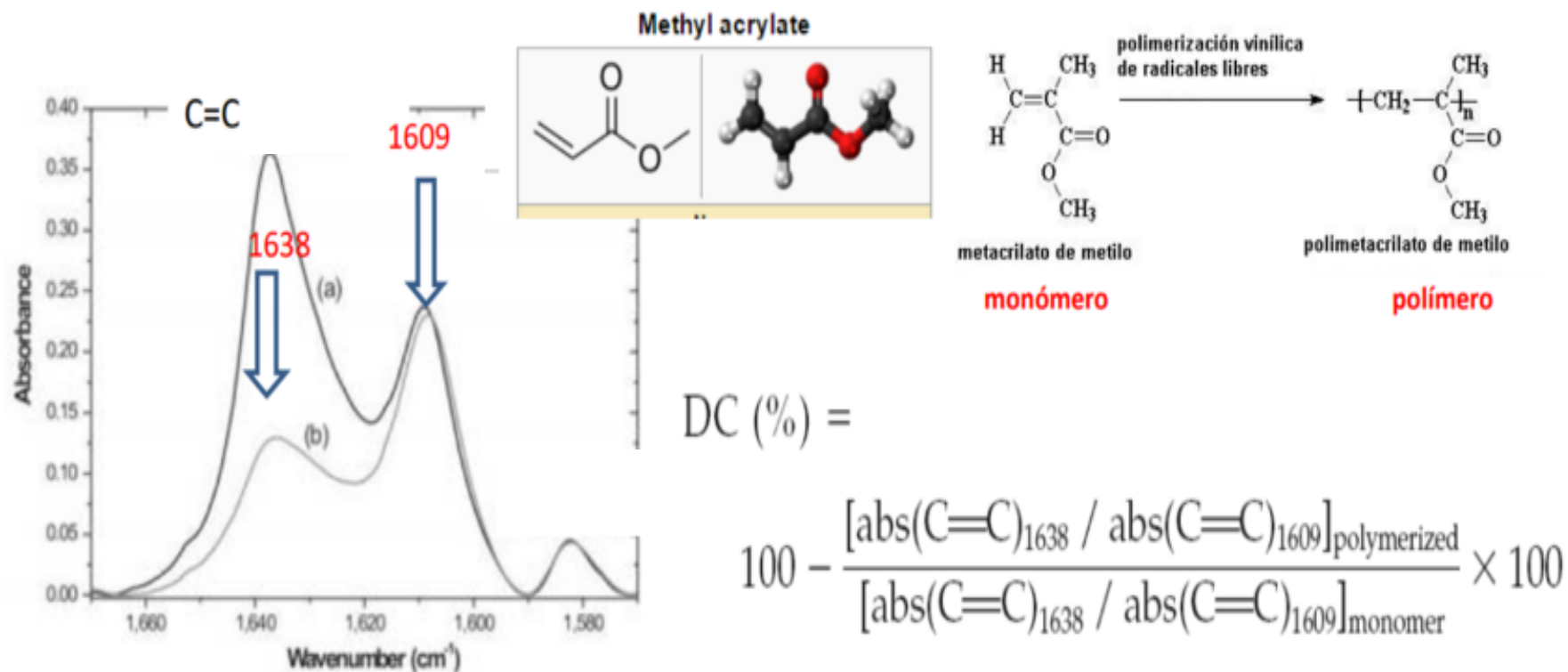


CO ₂	H ₂ O
 Raman: 1335 cm ⁻¹	 Raman + IR: 3657 cm ⁻¹
 IR: 2349 cm ⁻¹	 Raman + IR: 3756 cm ⁻¹
 IR: 667 cm ⁻¹	 Raman + IR: 1594 cm ⁻¹

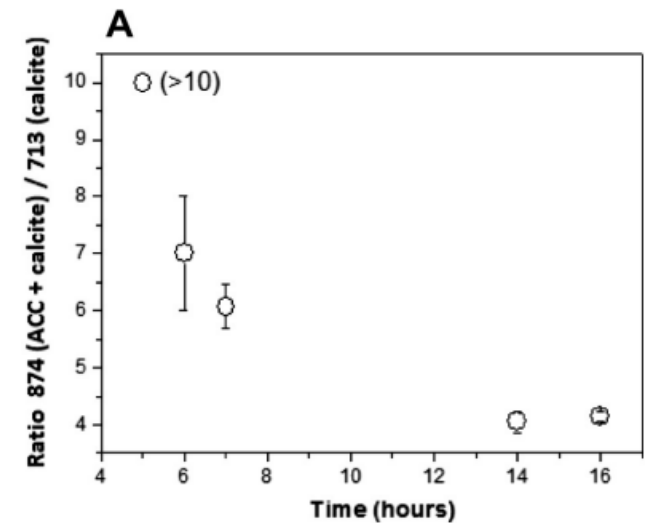
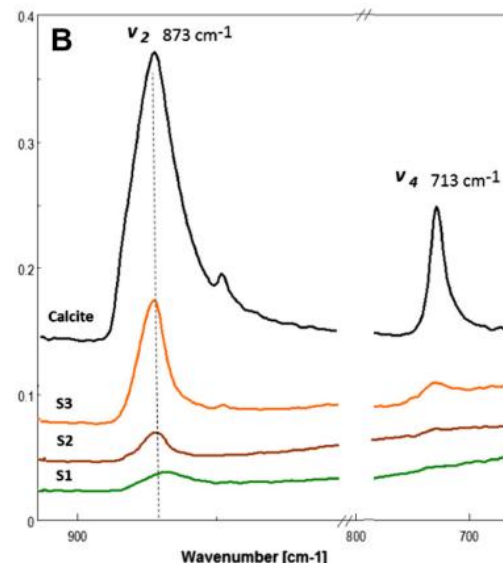
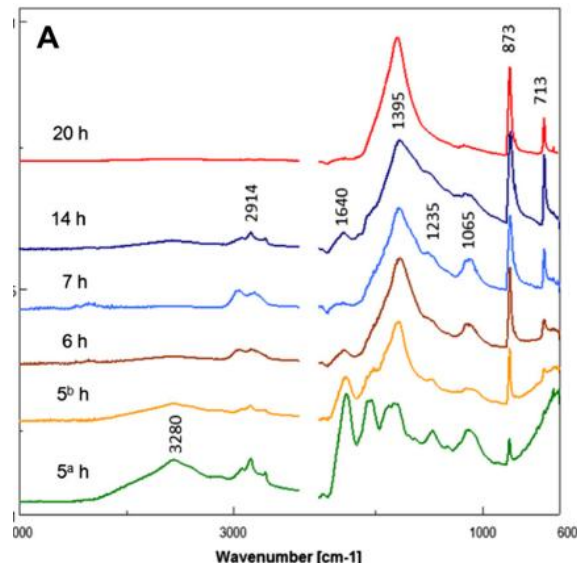
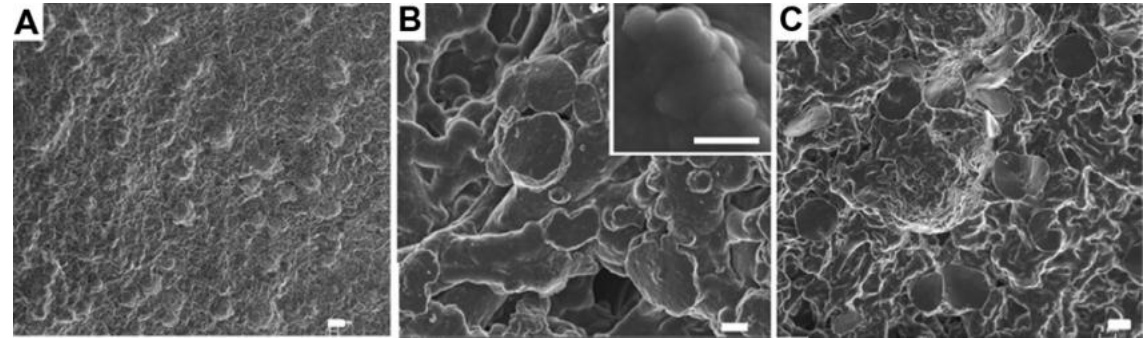
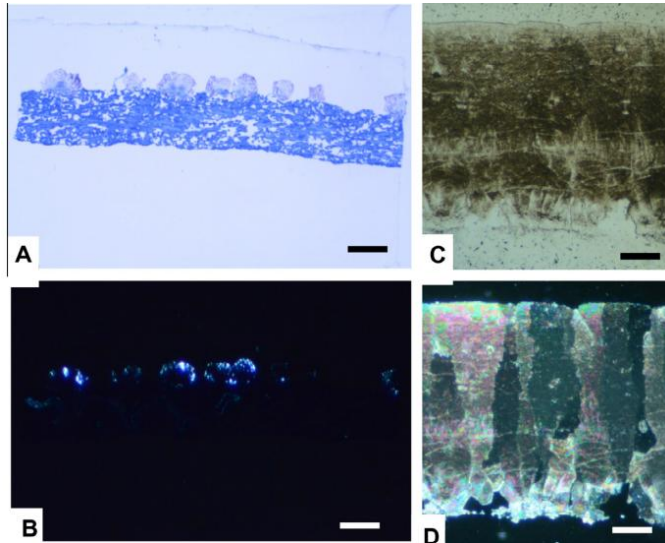


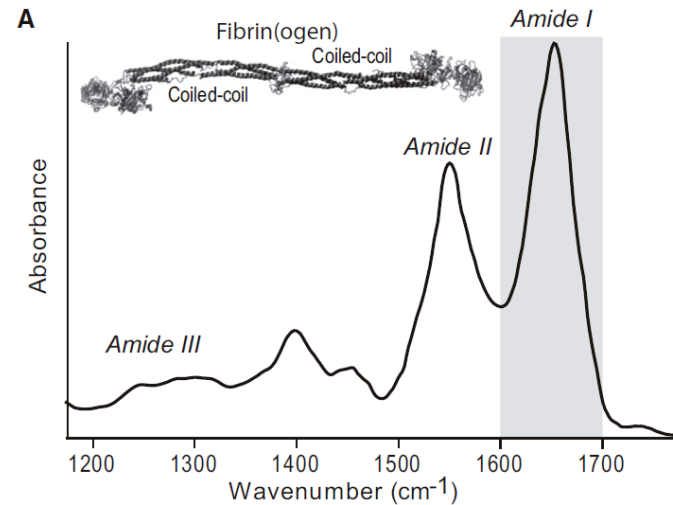
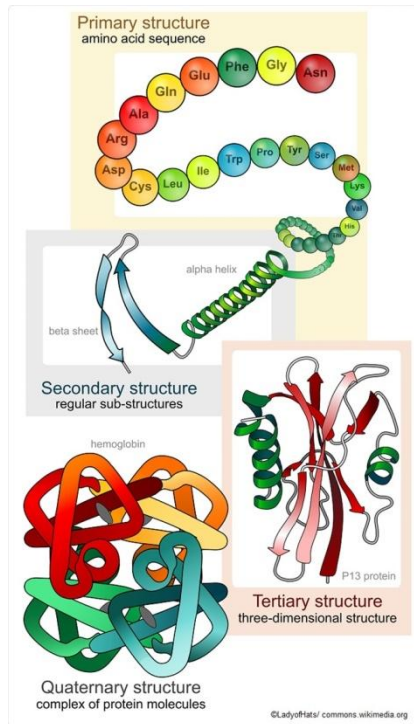
Application example 1: Polymerization reactions followed by IR

The degree of conversion (DC) can be monitored by the consumption of double bonds (C=C) in the monomer after polymerization

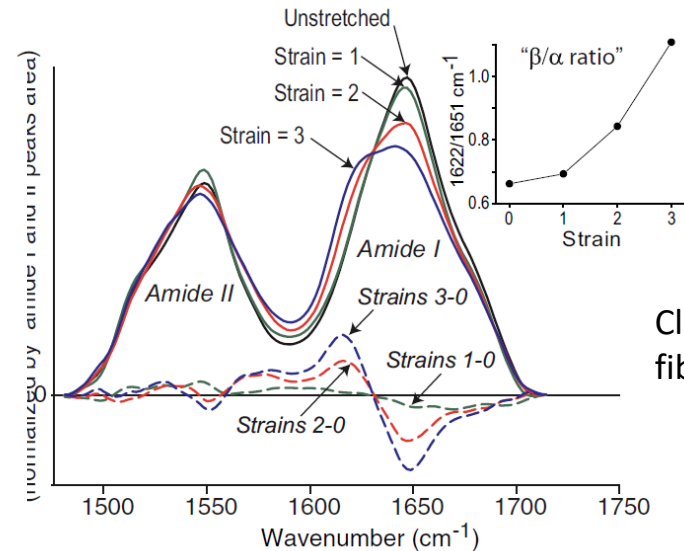
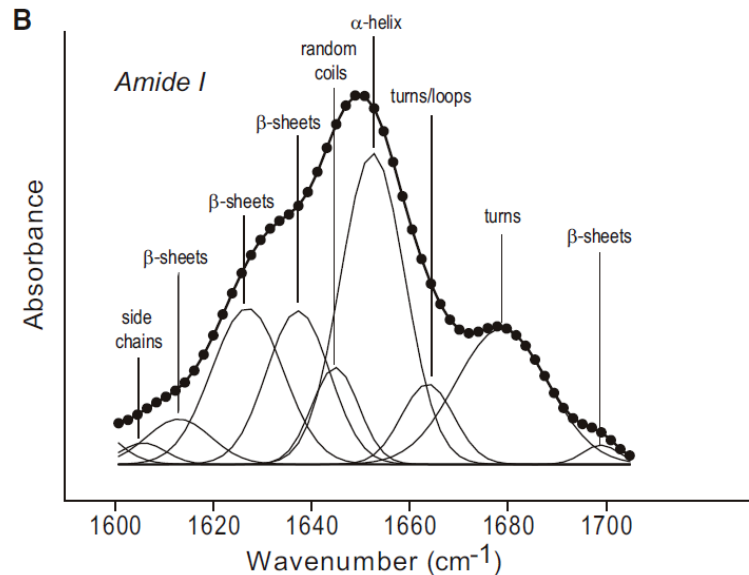


Example 2: Eggshell mineralization followed by IR



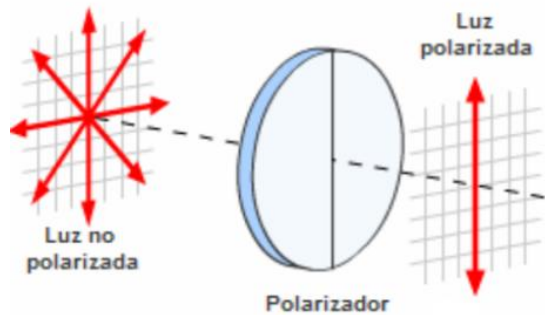


Secondary structure of proteins studied by FTIR (deconvolution of sub-bands amida I).

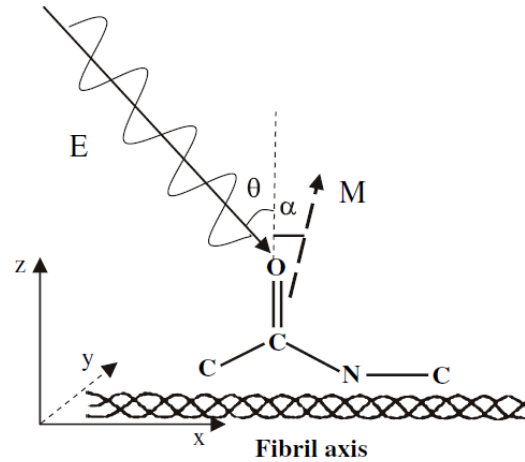


Clotting of
fibrinogen

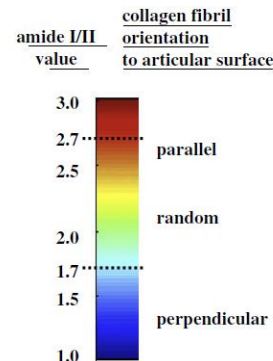
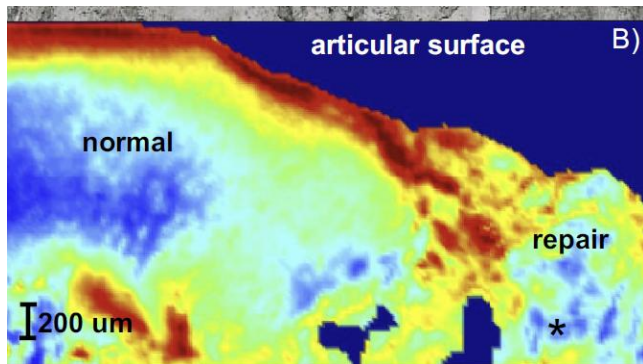
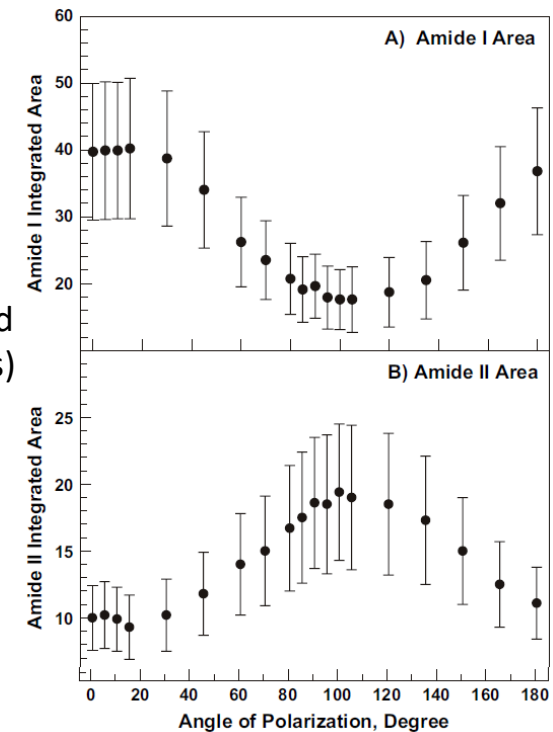
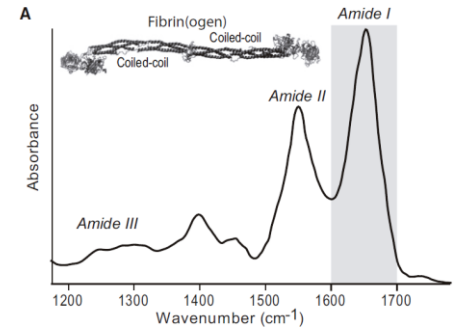
Example 4: Orientation of collagen molecules studied by IR



Polarized IR light

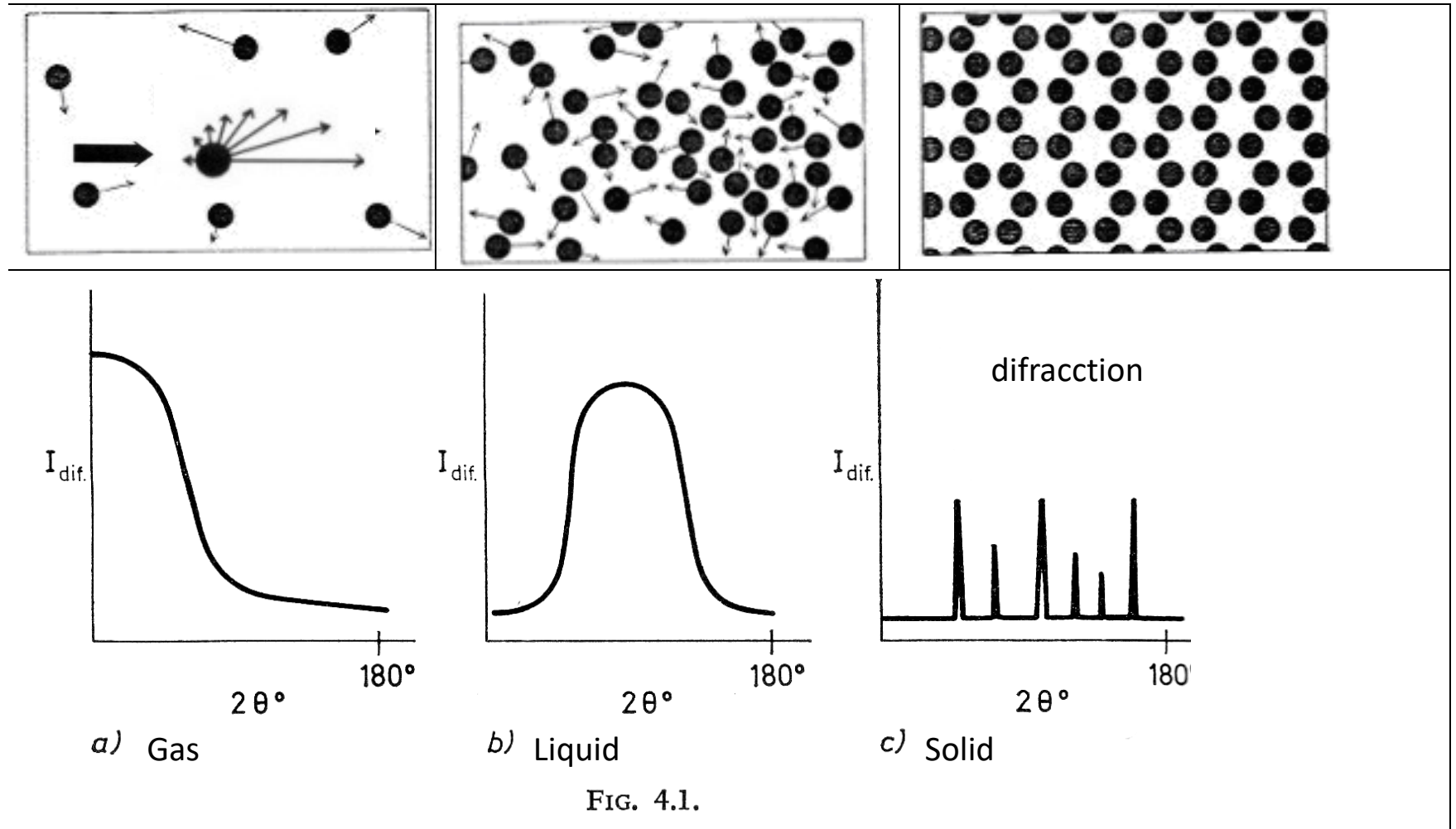


Collagen molecular groups amidas I and II (C=O, C-N) are ortogonal (90 degrees)

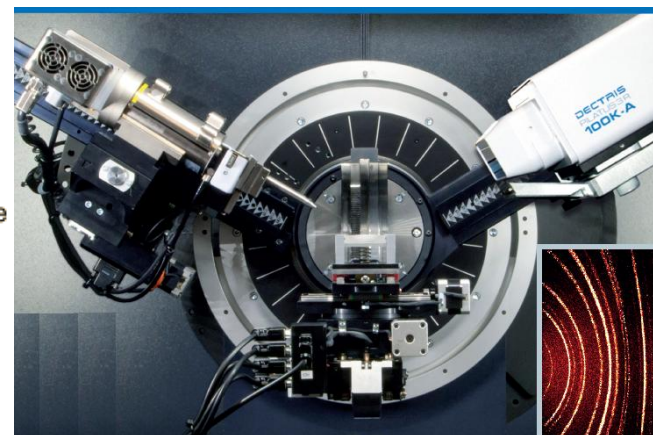
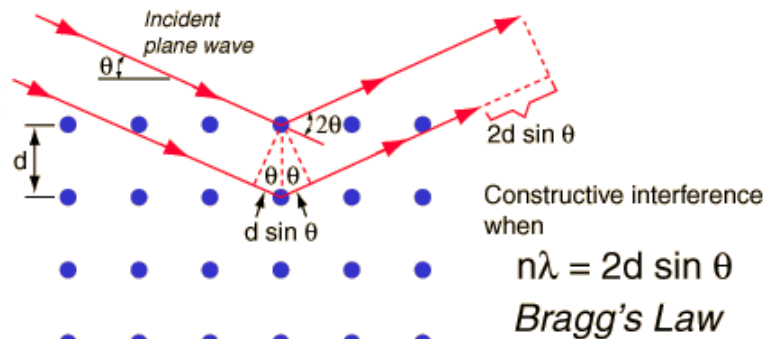


X-ray diffraction

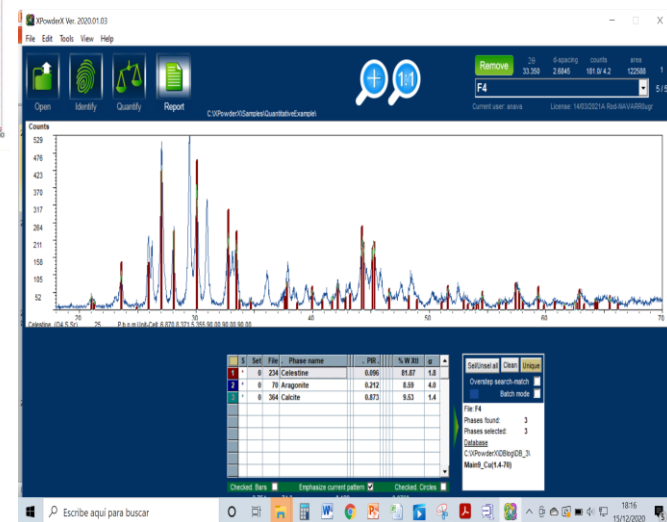
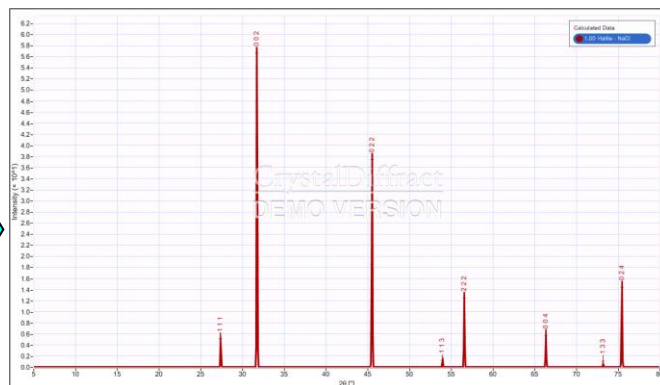
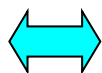
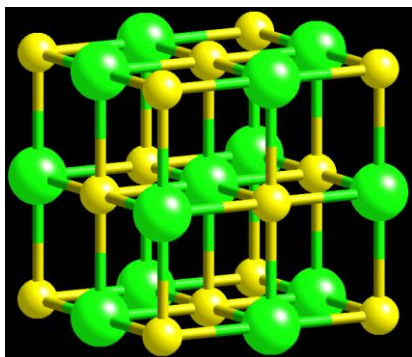
Scattering of X-rays by matter



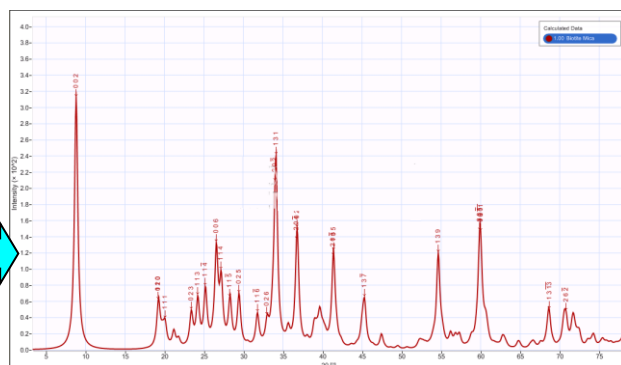
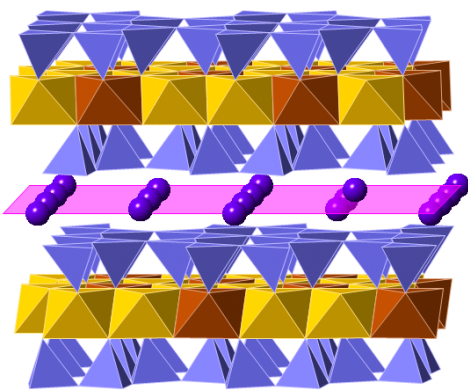
Example 1: Mineral identification by X-ray diffraction



Halita / Silvita

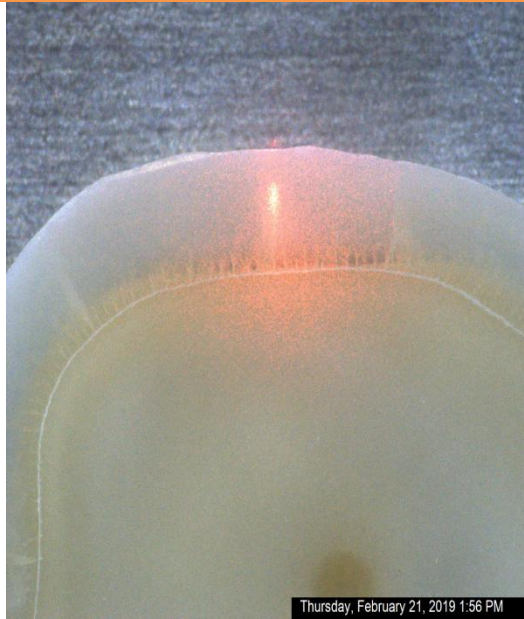


Biotita

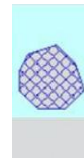
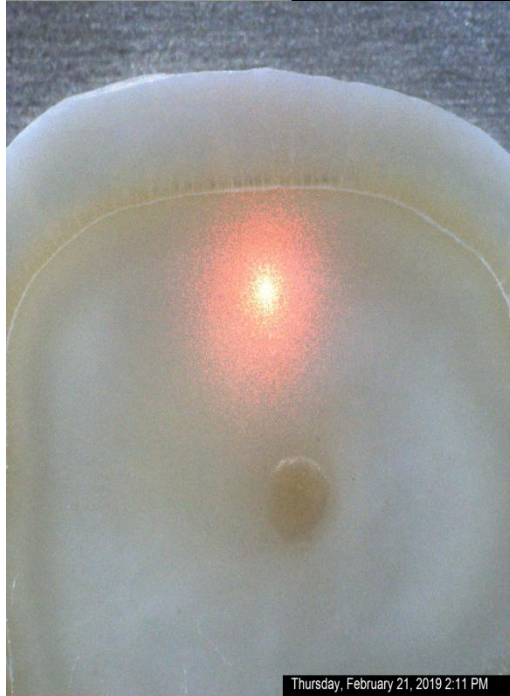
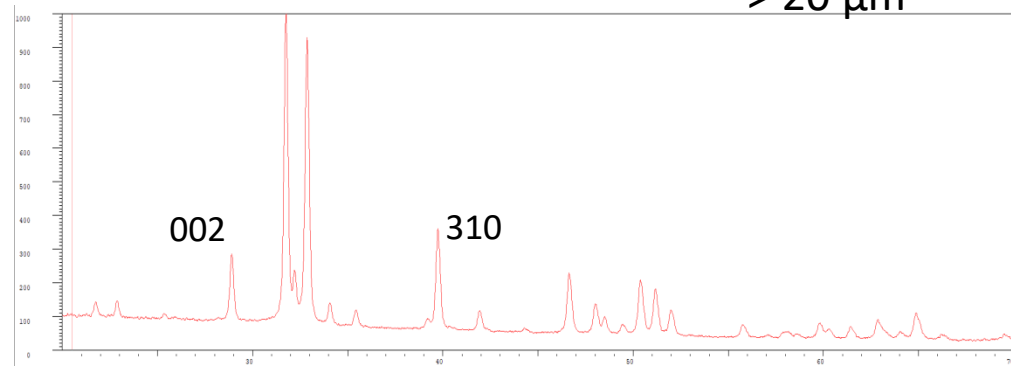


Mineral identification and quantification by XRD: High Score, Xpolder, Jade

Example 2: Nanocrystalline materials – particle size/crystallite size determination



Enamel
HAp highly crystalline
> 20 μm

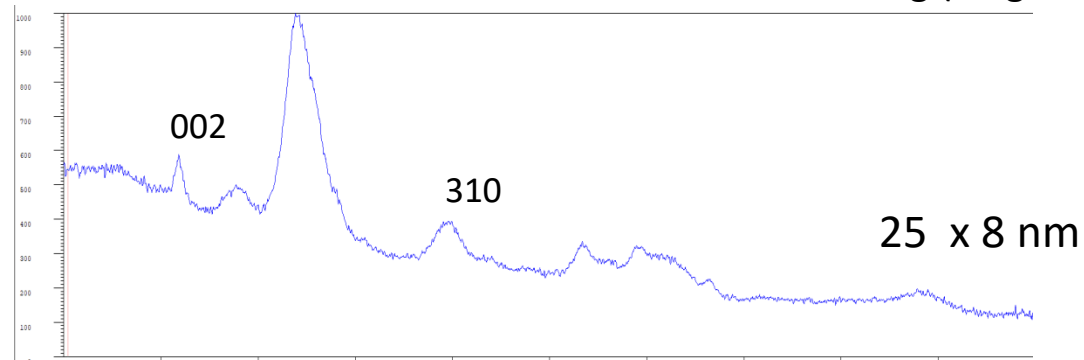


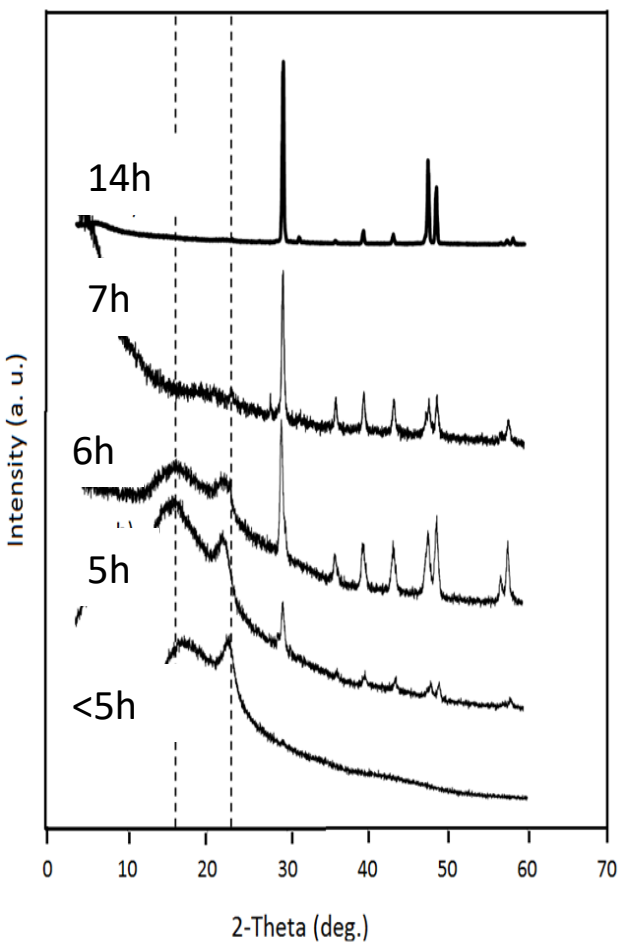
Scherrer
formula

$$t = \frac{K * \lambda}{B * \cos \theta_B}$$

Dentine
HAp poorly crystalline

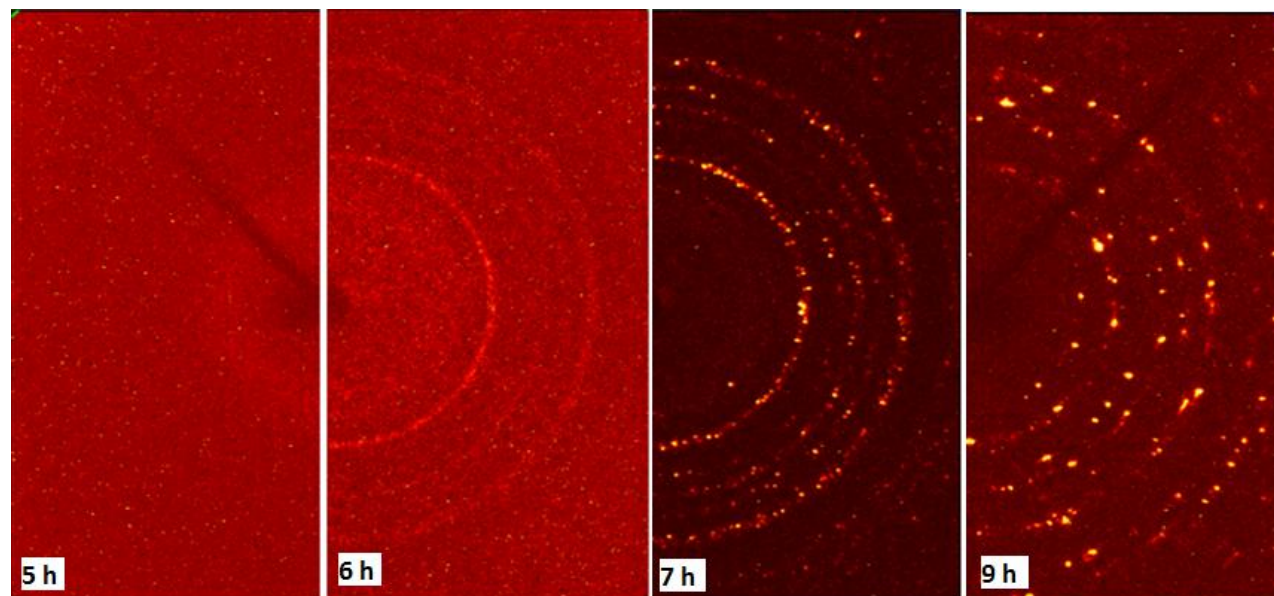
Anisotropic peak
broadening (length/width)





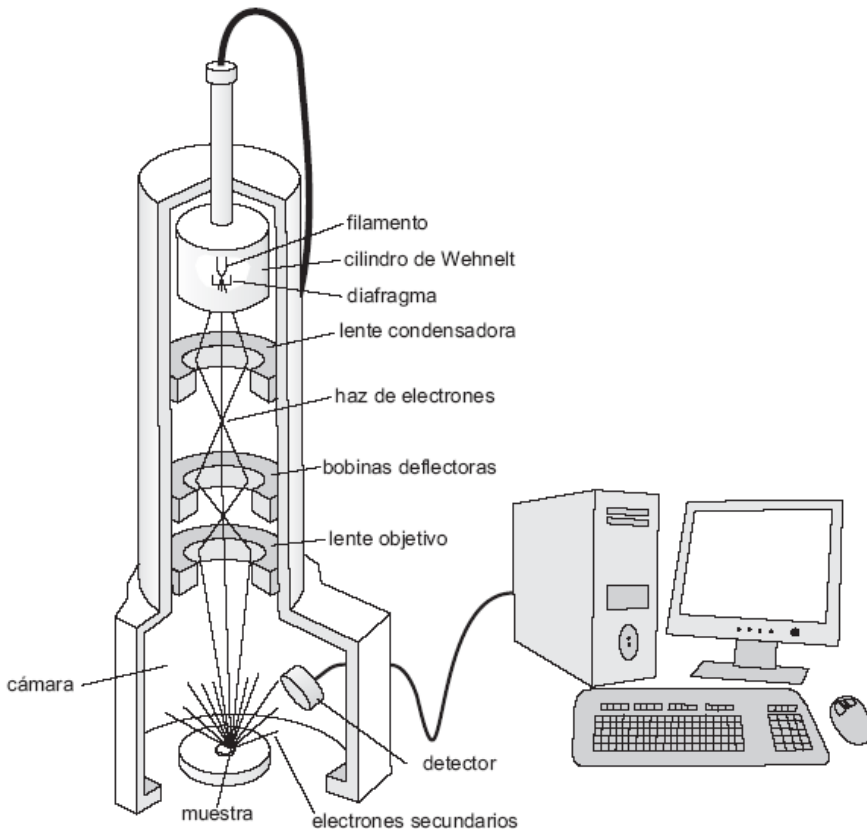
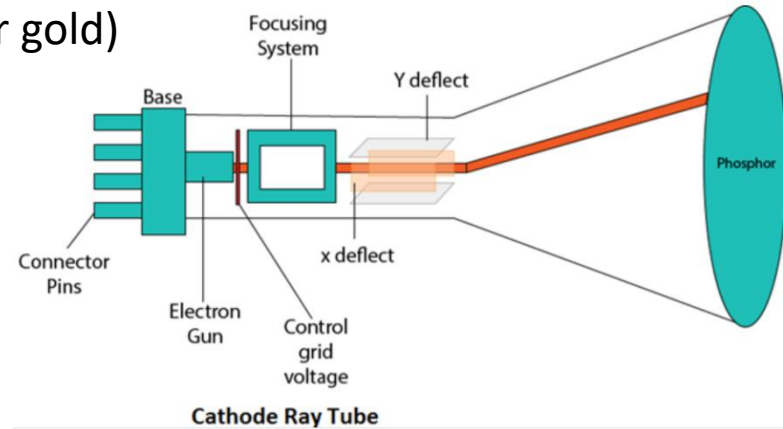
Conventional 1D scanning only show a increase in the **amount of calcite precipitating**.

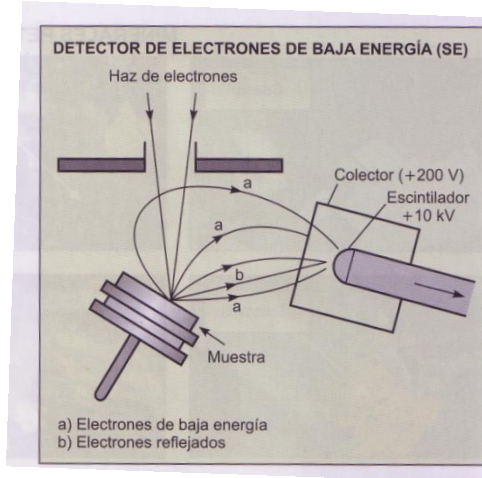
2D diffraction can see individual **crystal forming, dissolving and growing**.



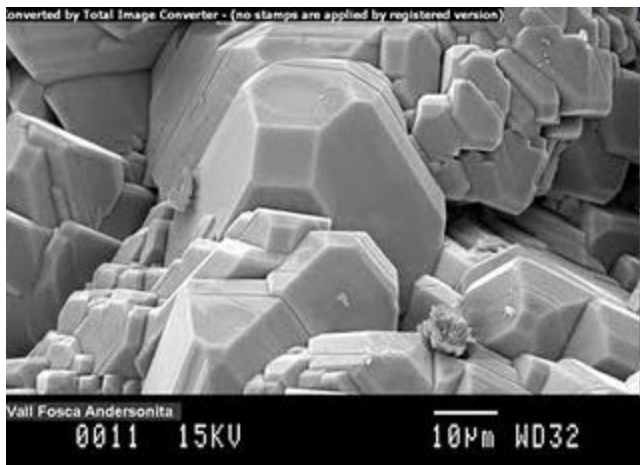
- Particle and surface (topography) analysis ($\times 20$ a $> \times 100.000$)
- High focal depth -3D images
- Resolution limit 1 nm
- Solid samples (conductive or coated with C or gold)

Acceleration voltage 2 a 30 kV

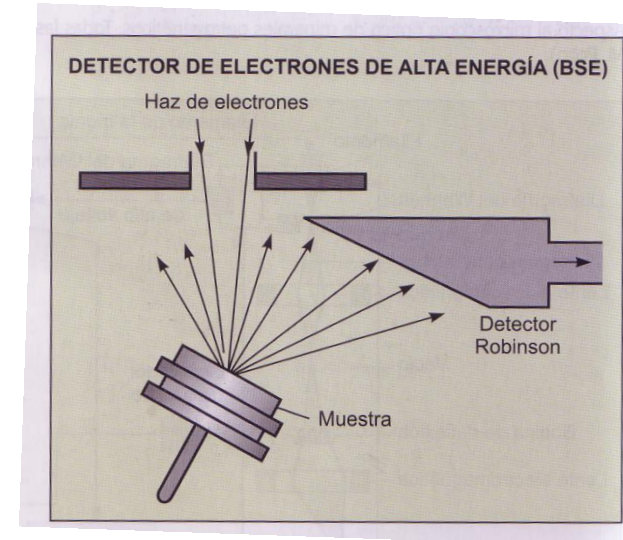




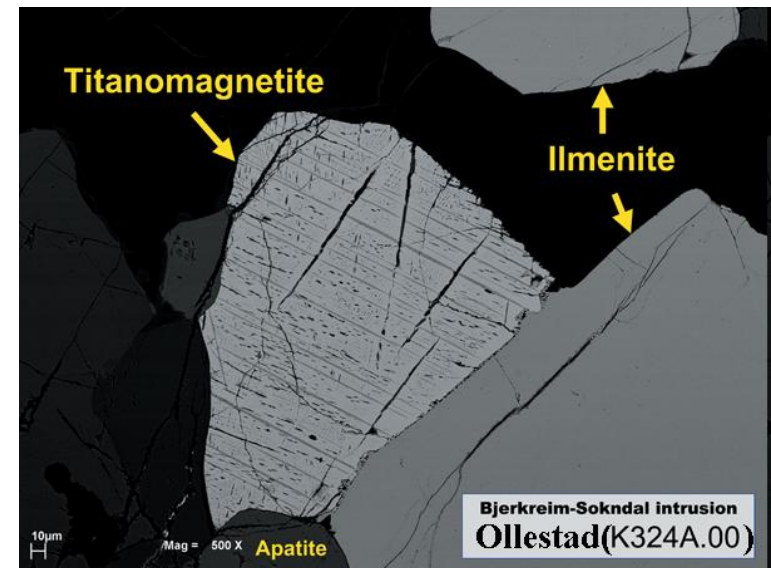
SE electrons - low energy

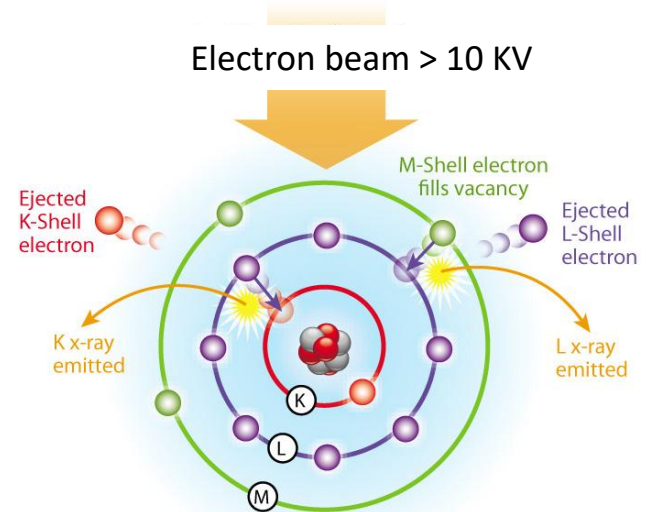
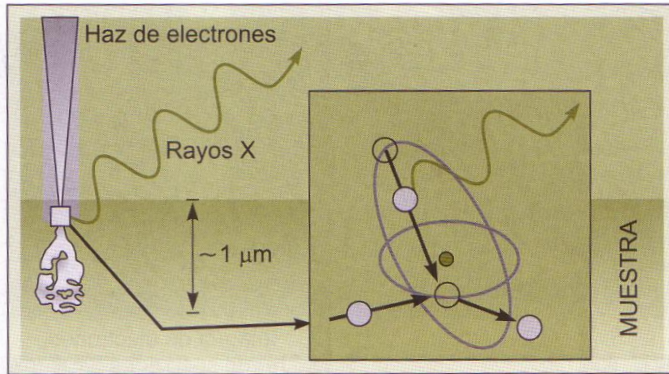


Andersonita

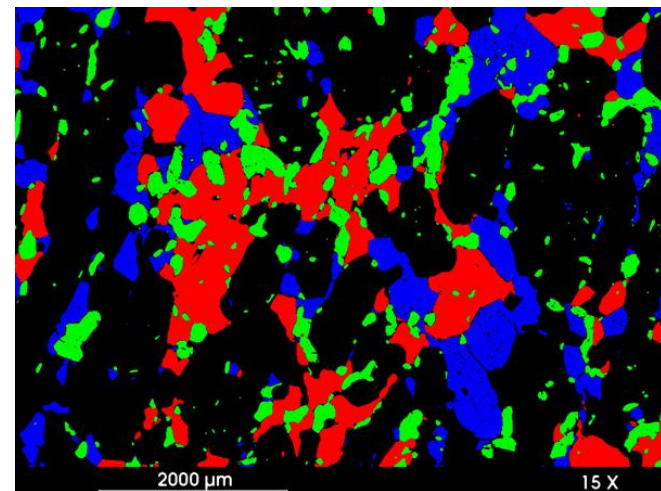
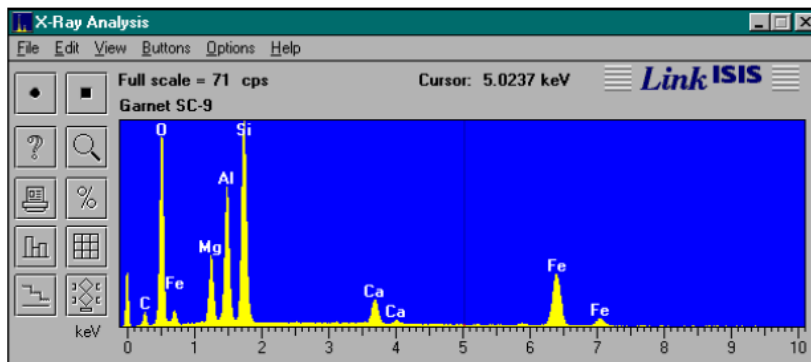


BSE electrons- high energy





Elemental map distribution



apatite (green), ilmenite (red) and magnetite (blue)

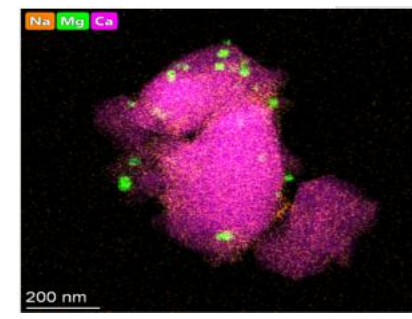
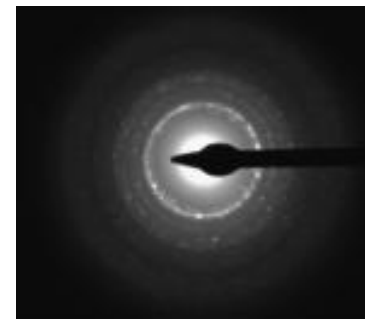
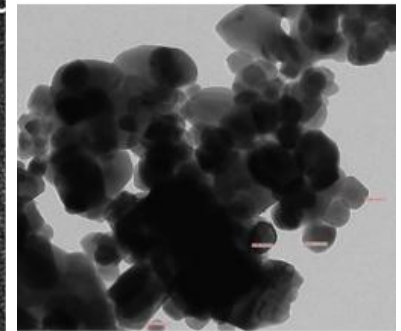
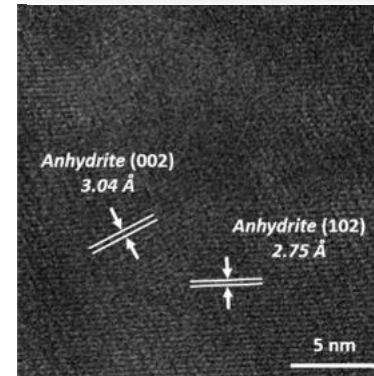
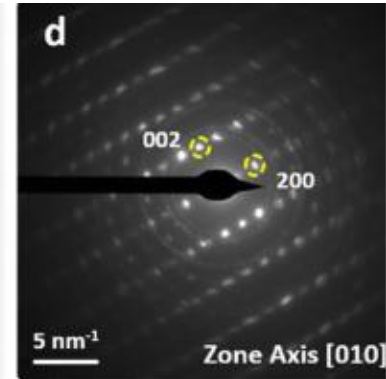
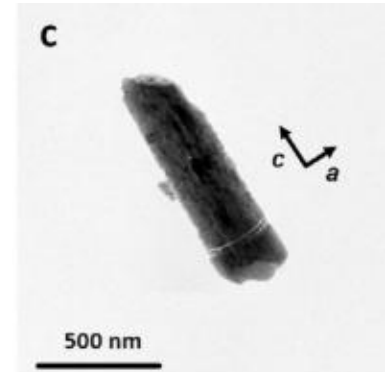
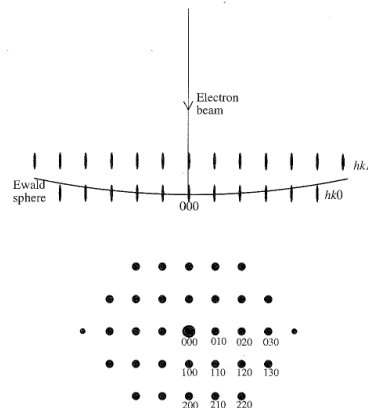
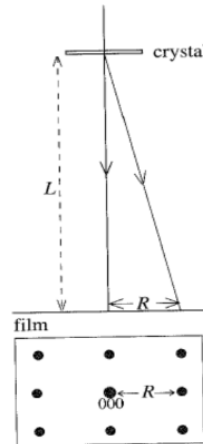
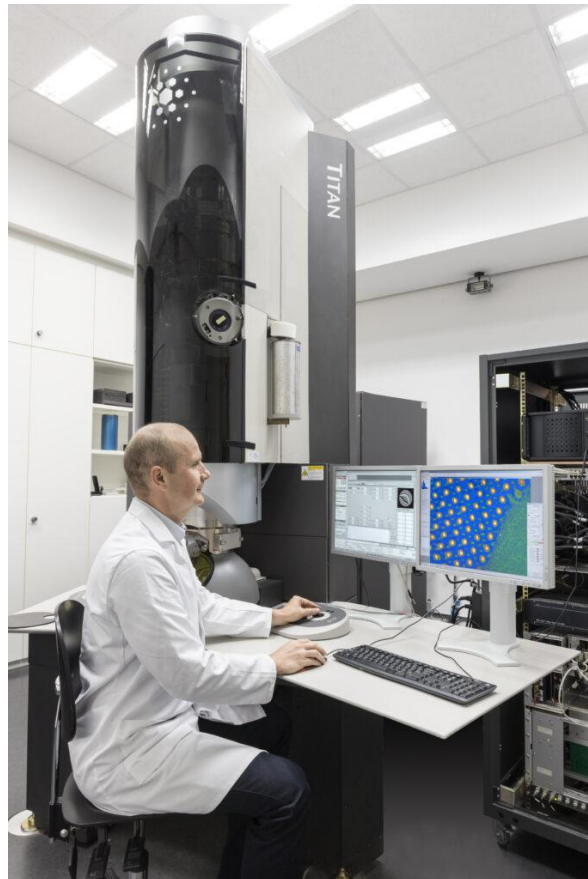
Transmission electron microscopy (TEM)

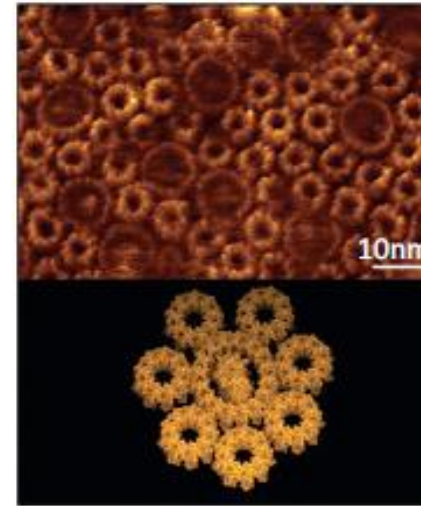
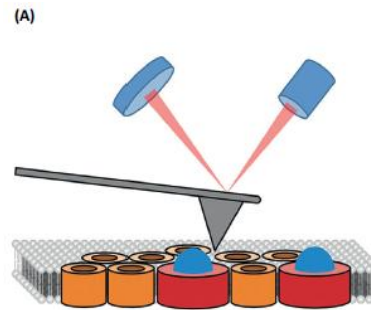
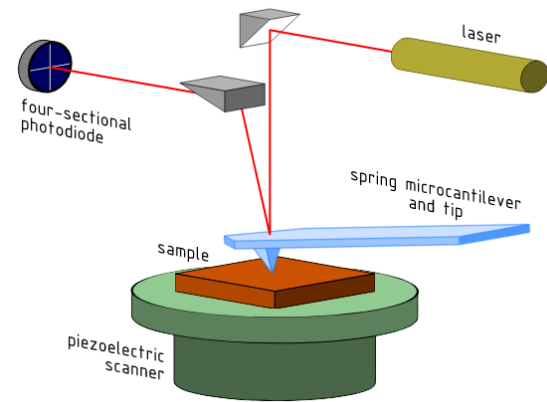
Nanoparticles (1-100 nm) or ultra thin sections (< 70nm).

< 0.1 nm resolution

Up to 300 KeV

Imaging + diffraction + chemical analyses (EDX, EELS)





Fotosintetic membrane image. Liu y Scheuring, 2013

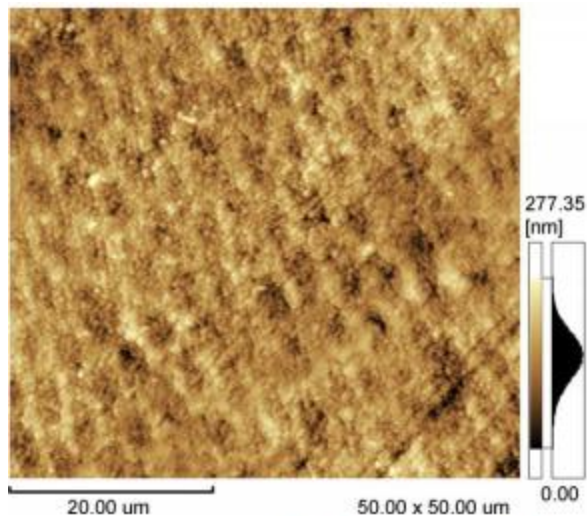


Fig. 1. AFM micrographs of bovine dental enamel, 50 μm x 50 μm

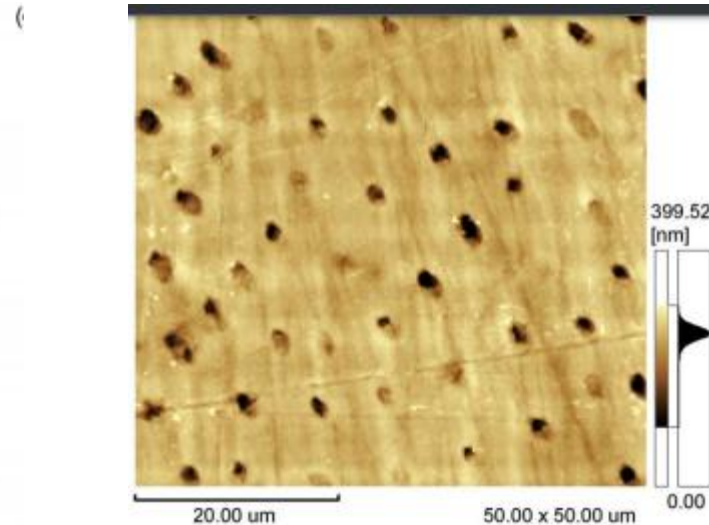
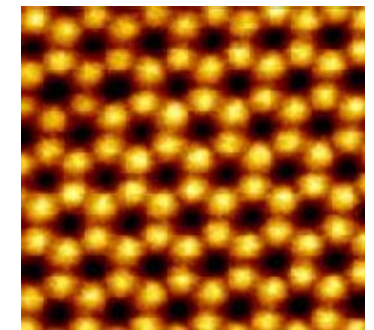
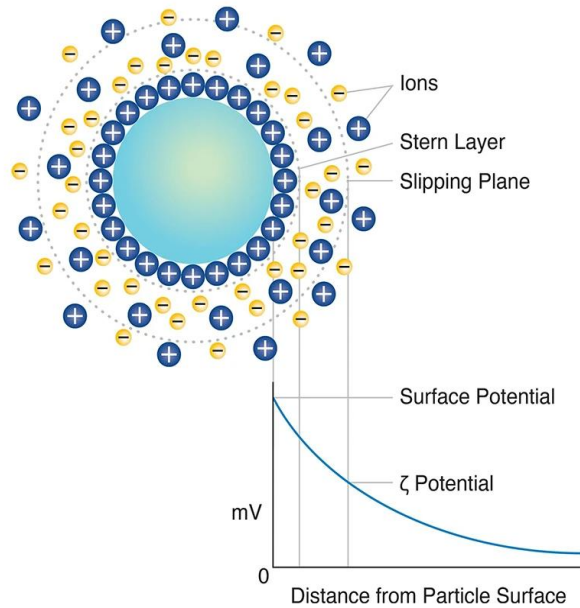


Fig. 3. AFM micrographs of bovine dentine, 50 μm x 50 μm

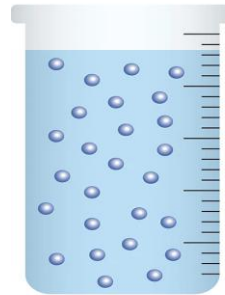


Silver crystal surface.
<http://www2.warwick.ac.uk/>

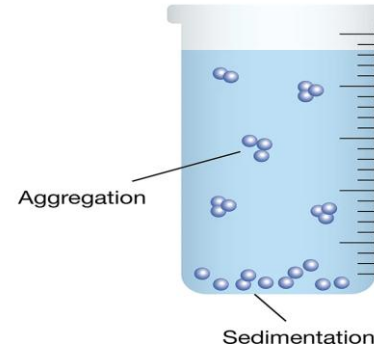
Surface properties - Zeta potential



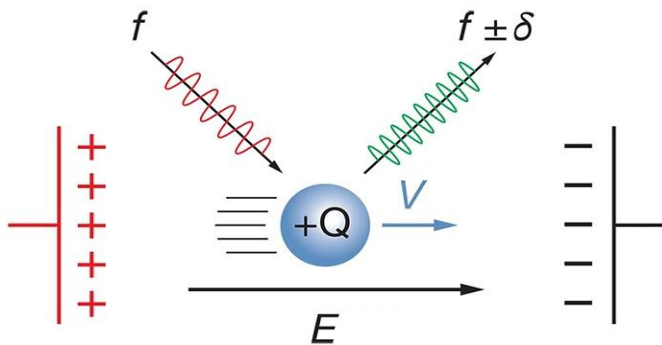
Stable Colloid
High Zeta Potential



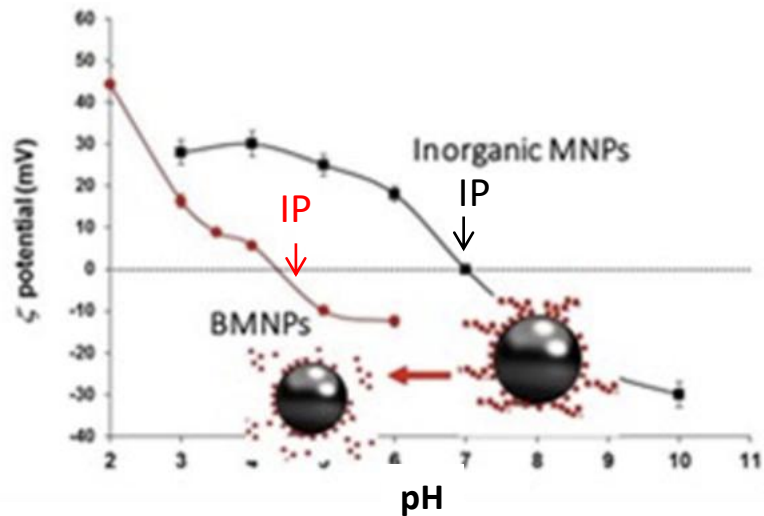
Unstable Colloid
Low Zeta Potential



Electric potential within the interfacial double layer (ions and counterions) around particles.
Determine the stability of colloidal/particle suspensions



Electrophoretic Light Scattering (ELS)
is used to measure the electrophoretic mobility of particles.



Zeta-potential of magnetic nanoparticles vs pH

Thanks !!