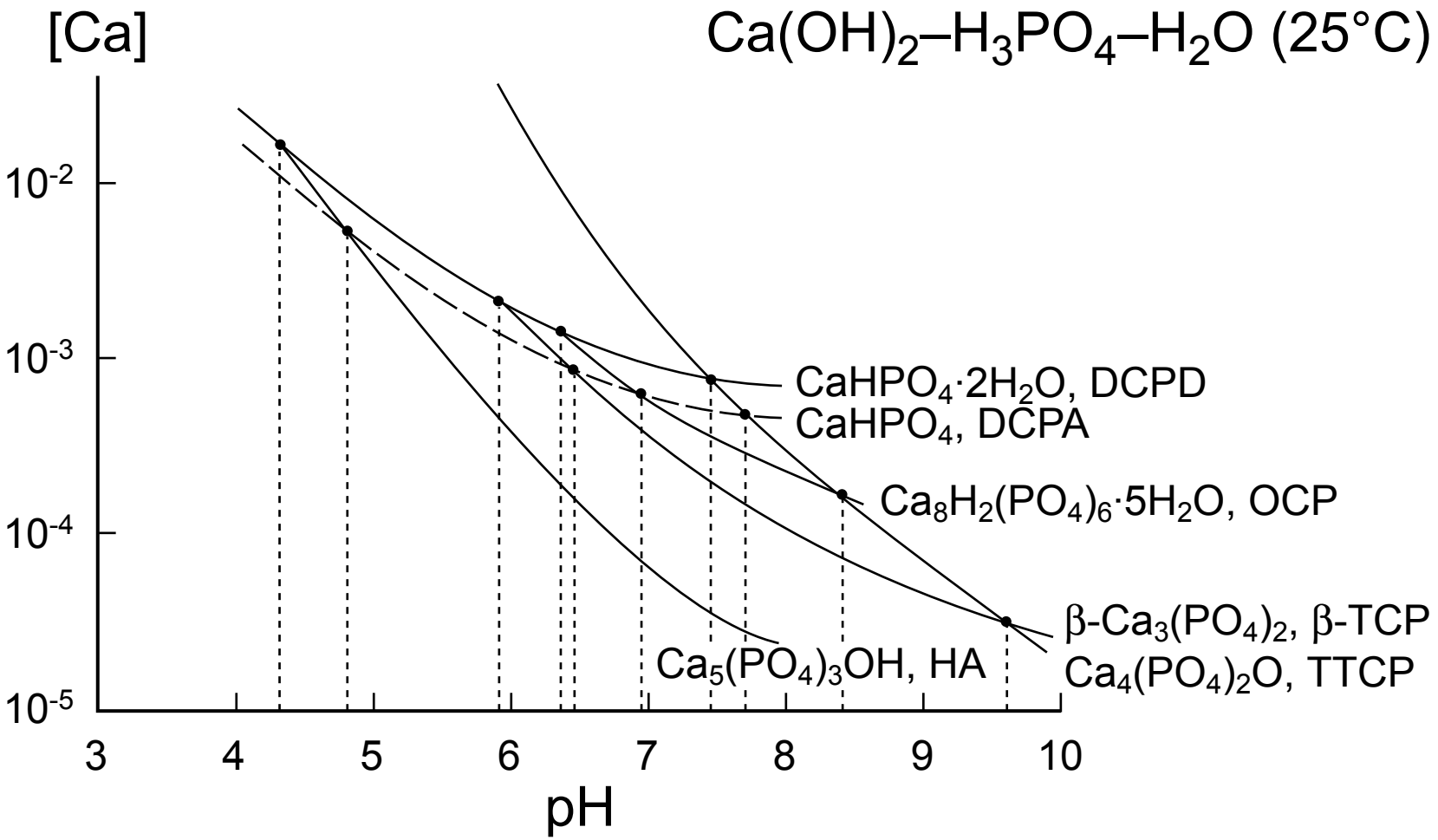
Calcium Orthophosphates

Ca/P	Abbreviation	Chemical Formula	Chemical Name	Mineral Name	-log (K_{sp})[1]	Crystal Structure
	CP, CaP		calcium phosphate (any)			
0.50	MCPA	$Ca(H_2PO_4)_2$	monocalcium phosphate, anhydrous		n/a[2]	triclinic
0.50	MCPM	$Ca(H_2PO_4)_2{\cdot}H_2O$	monocalcium phosphate monohydrate		n/a[2]	triclinic
1.00	DCPA	$CaHPO_4$	dicalcium phosphate, anhydrous	monetite	6.90	triclinic
1.00	DCPD	$CaHPO_4{\cdot}2H_2O$	dicalcium phosphate dihydrate	brushite	6.59	monoclinic
1.33	OCP	$Ca_8H_2(PO_4)_6{\cdot}5H_2O$	octacalcium phosphate		96.6	triclinic
≤1.50	ACP		amorphous calcium phosphate		n/a[2]	amorphous
1.50	α-TCP	α-$Ca_3(PO_4)_2$	alpha-tricalcium phosphate		25.5	monoclinic
1.50	β-TCP	β-$Ca_3(PO_4)_2$	beta-tricalcium phosphate	whitlockite (+Mg)	28.9	rhombohedral
	BCP		biphasic calcium phosphate[3]			
1.67	HAp, HA, OHAp	$Ca_{10}(PO_4)_6(OH)_2$	calcium hydroxyapatite	hydroxyapatite	58.4	hexagonal
1.67	FAp	$Ca_{10}(PO_4)_6F_2$	calcium fluoroapatite	fluoroapatite	60.5	hexagonal
1.67	ClAp	$Ca_{10}(PO_4)_6Cl_2$	calcium chloroapatite	chloroapatite		hexagonal
≈1.67	CO_3Ap, CO_3-HA	$Ca_{10}(PO_4)_6(OH)_{2-2x}(CO_3)_x$[4]	carbonated hydroxyapatite	dahllite		hexagonal
2.00	TTCP or TetCP	$Ca_4(PO_4)_2O$	tetracalcium phosphate	hilgenstockite	38.0	monoclinic

[1] Measured at 25°C.
[2] Highly soluble.
[3] A mixture of HA and β-TCP used to tailor bioactivity.
[4] A-type carbonate substitution for hydroxyls is shown. Carbonate may also substitute for phosphate (B-type). Therefore, a more general chemical formula for A- or B-type substitution is $Ca_{10-2x/3}(PO_4)_{6-x}(CO_3)_x(OH)_{2-x/3}$.

Calcium Phosphate Solubility Diagram



Adapted from W.E. Brown, *Clin. Orthop.*, 1966.

Cortical Bone Composition

I. aqueous body fluid (≈33 vol%)
    A. water/ions
    B. cells
    C. proteins

II. extracellular matrix (ECM) (≈67 vol%)

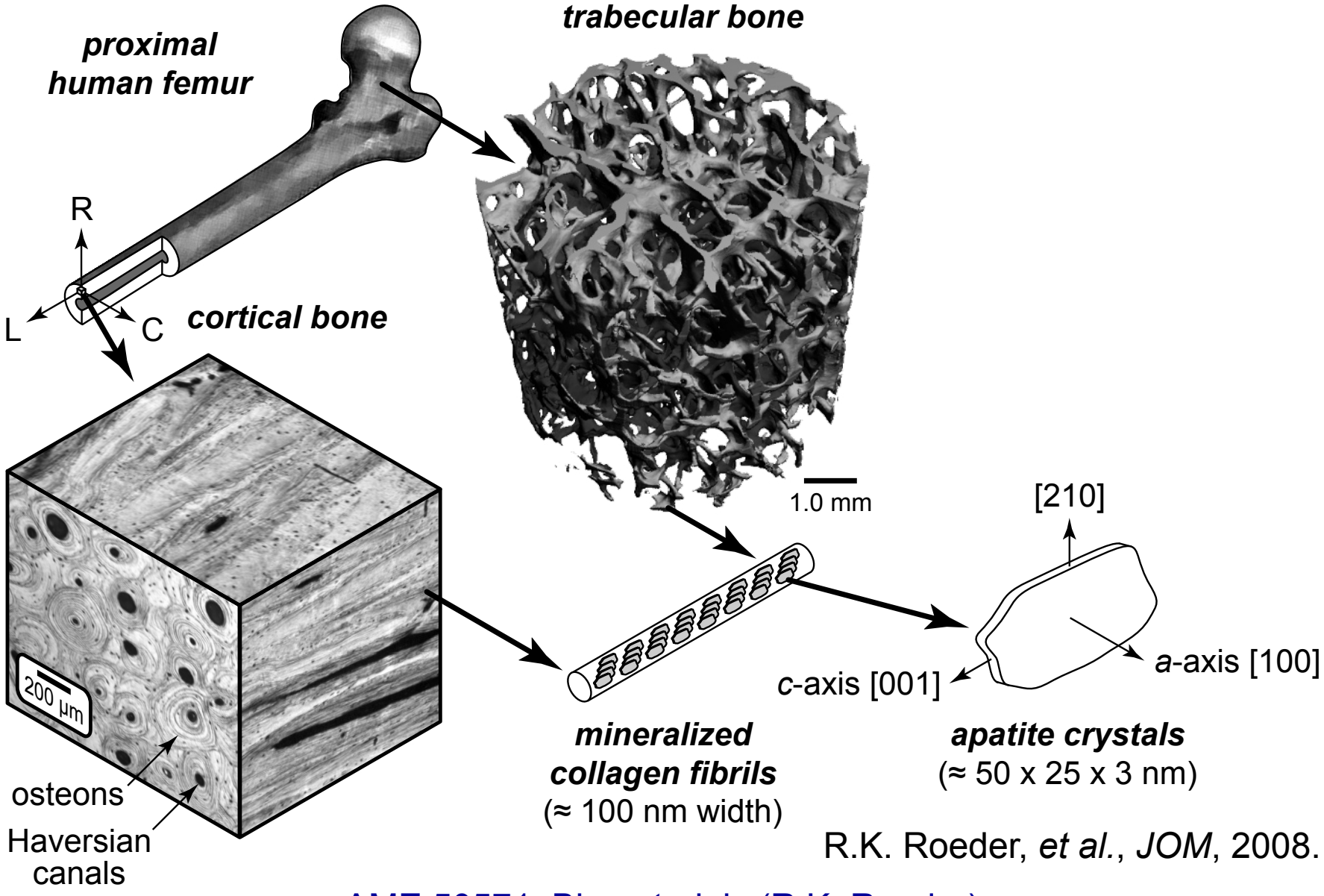
structurally...

    A. interstitial bone (≈33 vol%)
    B. osteons or Haversian systems (≈67 vol%)

compositionally...

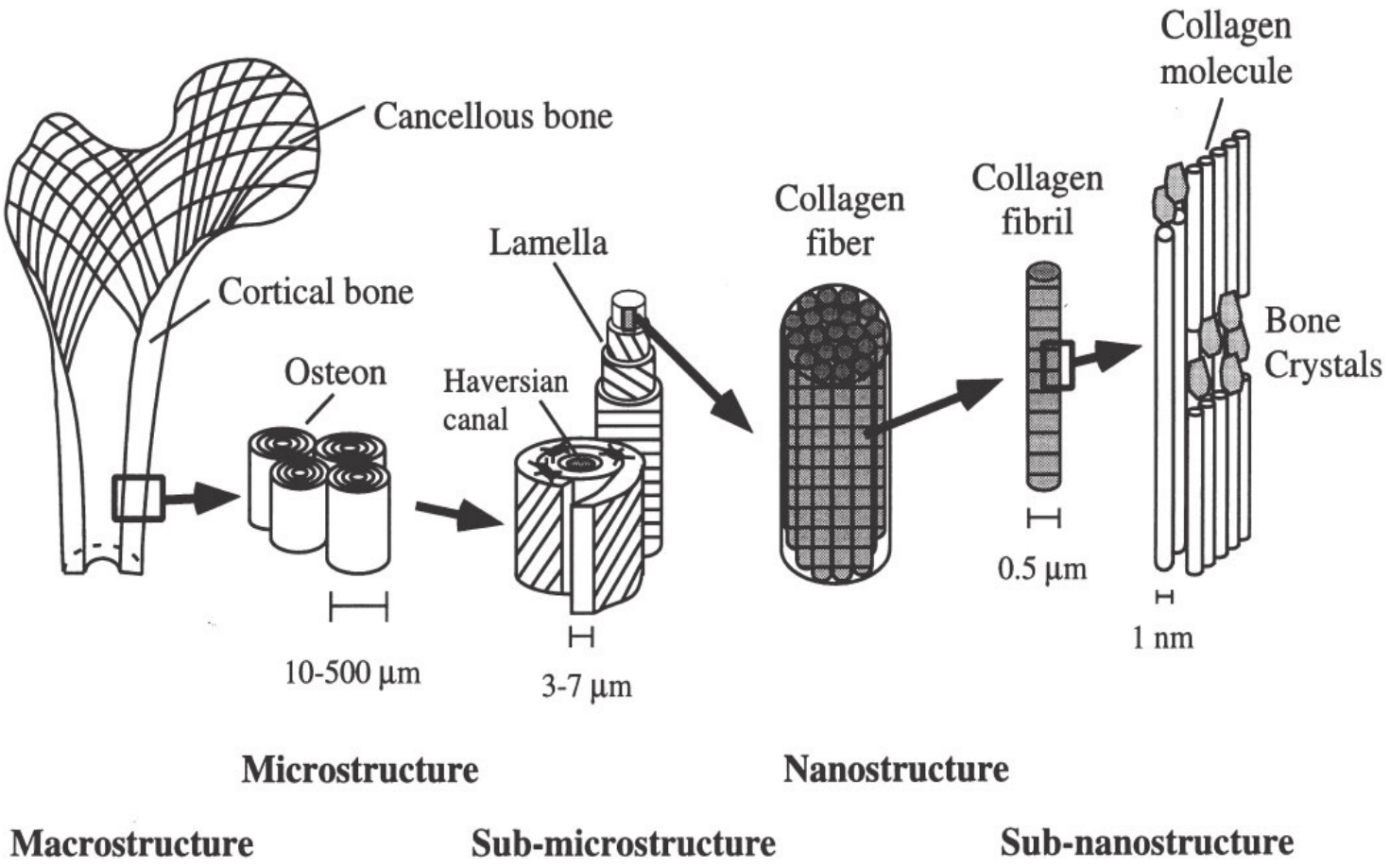
    A. organic-osteoid (≈50 vol% or ≈30 wt%)
        1. collagen (≈90 vol%)
        2. non-collagenous proteins (≈10 vol%)
    B. inorganic-apatite (≈50 vol% or ≈70 wt%)

Hierarchical Structure of Bone Tissue



R.K. Roeder, *et al.*, *JOM*, 2008.

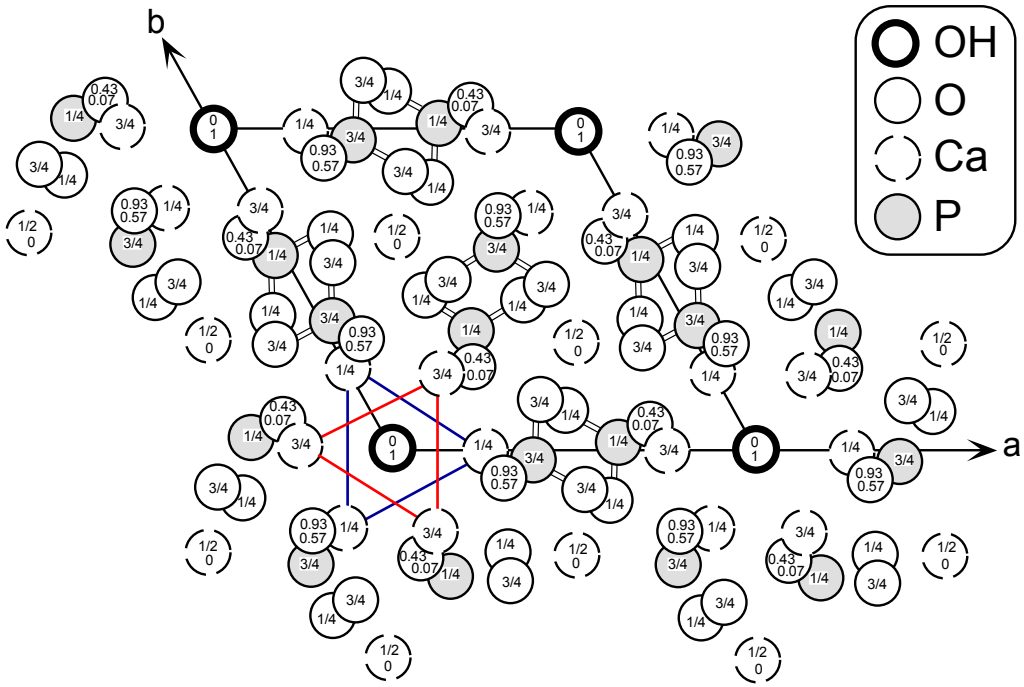
Hierarchical Structure of Bone Tissue



J-Y. Rho, *et al.*, *Med. Eng. Phys.*,1998.

Hydroxyapatite Crystal Structure

$Ca_{10}(PO_4)(OH)_2$
space group: $P6_3/m$



Bone Mineral

- calcium deficient
- highly substituted
- low crystallinity

Adapted from Young and Elliott, *Archs. Oral. Biol.*, 1966.

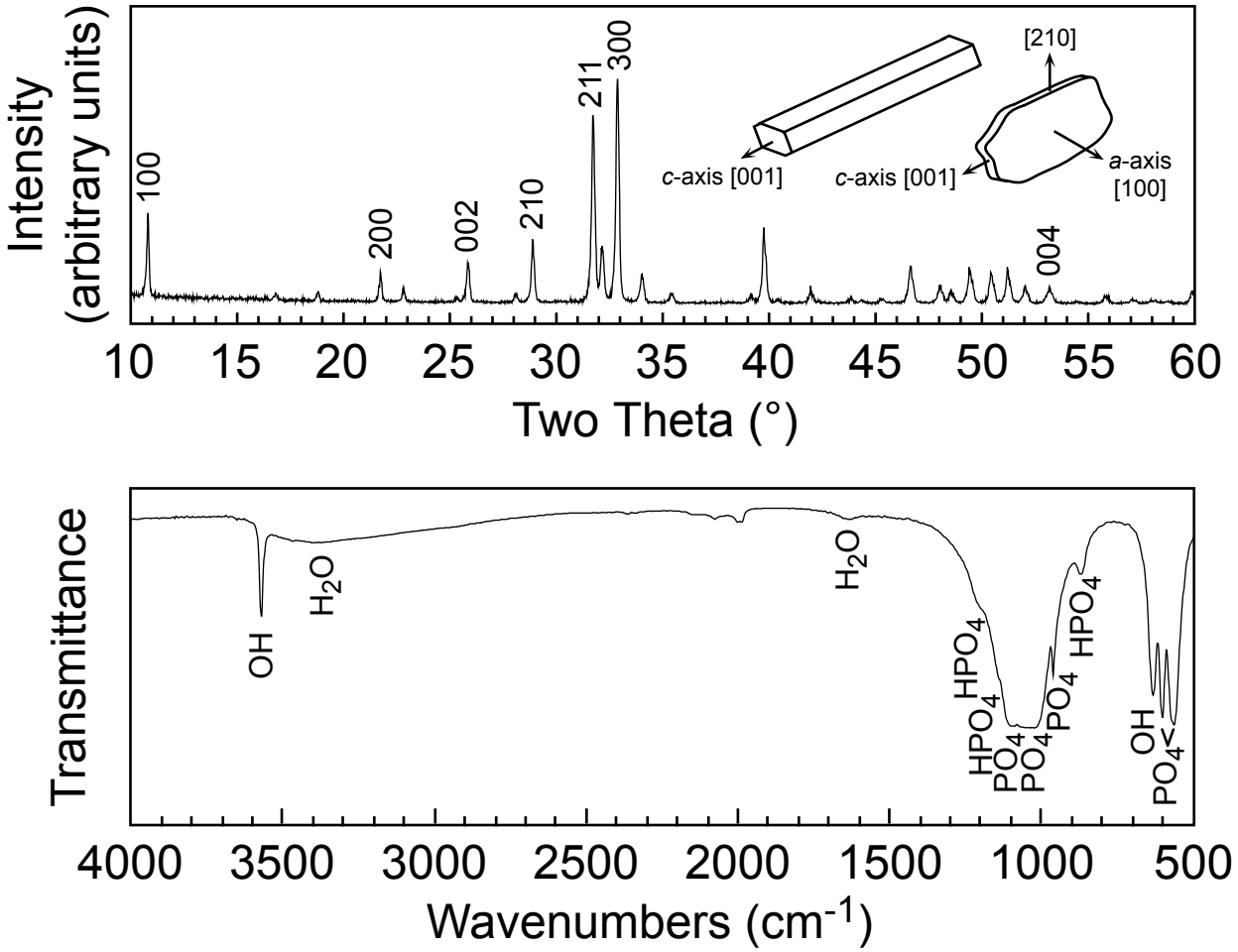
Bone Mineral Composition

$(Ca,M)_{10}(PO_4,CO_3,Y)_6(OH,Cl,F)_2$ where M = Mg^{2+}, Na^{+}, K^{+}...
Y = HPO_4^{2-}, SO_4^{2-}...

Consitituents (wt%)	Cortical Bone	Synthetic HA
calcium, Ca^{2+}	24.50	39.60
phosphorus, P in PO_4^{3-}	11.50	18.50
Ca/P molar ratio	1.65	1.67
sodium, Na^{+}	0.70	trace
potassium, K^{+}	0.03	trace
magnesium, Mg^{2+}	0.55	trace
carbonate, CO_3^{2-}	5.80	–
fluoride, F^{-}	0.02	–
chloride, Cl^{-}	0.10	–
ash (total inorganic)	65.00	100
total organic	25.00	–
adsorbed H_2O	9.70	–

Adapted from R.Z. LeGeros., *Prog. Cryst. Growth Charact.*, 1981.

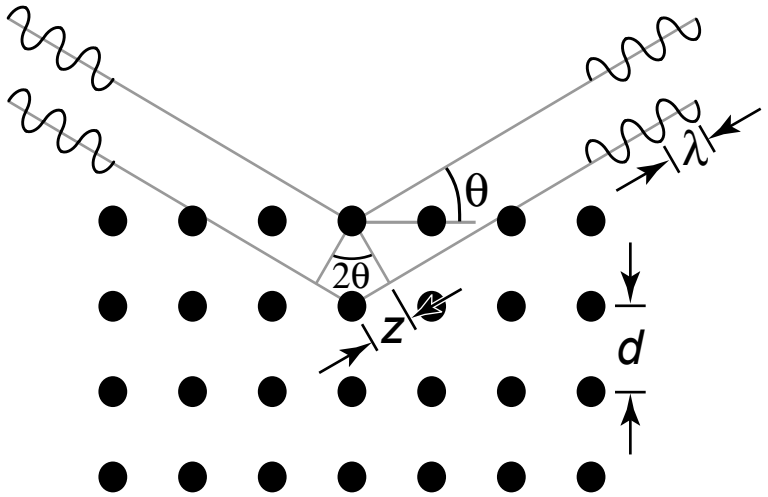
XRD and FT-IR Spectra for HA



Adapted from Roeder *et al.*, *J. Am. Ceram. Soc.*, 2006.

XRD Spectra

x-ray detector



x-ray source: Cu Kα radiation (λ = 1.54 Å)

- monochromatic
- parallel
- coherent (in phase)

constructive interference requires:

$n \cdot \lambda = 2z$ where $z = d \cdot \sin\theta$

Bragg's Law: $n \cdot \lambda = 2d \cdot \sin\theta$

where d = interplanar spacing

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{(cubic)}$$

a = lattice parameter

hkl = Miller indices

used predominately in inorganic crystalline materials to determine:

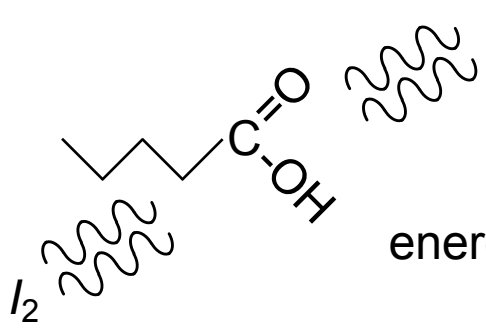
- phase identification (crystal structure)
- composition (phase fractions)
- crystal size → $t = \frac{0.9\lambda}{B \cdot \sin\theta}$
- lattice parameters
- crystal orientation (texture analysis)
- residual stresses

where $B^2 = B_m^2 - B_s^2$

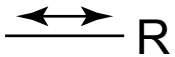
B_m = peak breadth measured at one-half the max. intensity

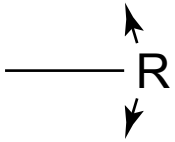
B_s = that of a ref. material with crystal size > 0.1 μm

FT-IR Spectra



energy is absorbed by characteristic molecular vibrations

e.g., stretching  R

bending  R

etc.

used predominately in organic molecules and macromolecules to determine:

- ligand identification (molecular structure)
- composition