Innovative Technologies and Sustainable Use of Mediterranean Sea Fishery and Biological Resources
(FishMed-PhD 37 2022-03-01)

Crystallization in Environment and Environmental Protection

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1. Kinetics and Mechanisms of Crystallization Processes

Crystallization or Precipitation??

Precipitation = Physical-chemical process of formation of new phase in homogeneous system

Liquid in gas (rain droplets in air - clouds)

Gas in liquid (CO_2 bubbles)

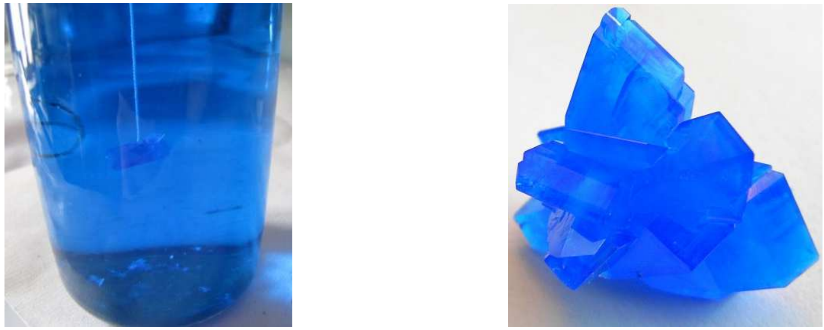
Solid in gas (smoke)

Solid in liquid (crystals in suspension)
(Precipitation in limited sense!!)

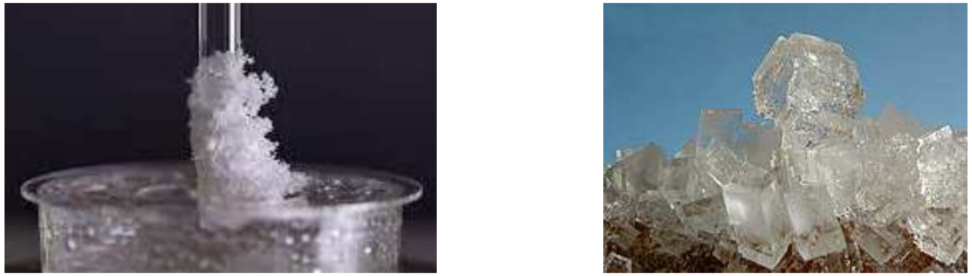
Illustrations from: M. S. Silberberg, Chemistry – The molecular Nature of Matter and Change, Fourth Edition, McGrow-Hill, 2006

Crystallization - examples

- $CuSO_4{\cdot}5H_2O$ - Copper sulfate pentahydrate (Blue vitriol)
- Evaporation of saturated solution
- solubility = 10.4 g/L
- large crystals



- NaCl – Sodium Chloride (Common salt)
- Evaporation of saturated solution
- solubility = 360 g/L
- large crystals



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Precipitation - examples

- AgCl - Silver chloride (chloride determination in water)
- Mixing of diluted $AgNO_3$ and NaCl solutions

  (Analytical chemistry: $Ag^+(aq) + Cl^-(ag) \leftrightarrow AgCl(s)$)
- Solubility = 5.2 mg/L (50 °C)
- micron-sized particles

- Silver chromate Ag_2CrO_4 (Mohr's method, indicator)
- Mixing of diluted $AgNO_3$ and K_2CrO4 solutions

  (Analytical chemistry: $2Ag^+(aq) + CrO_4^-(aq) Ag_2CrO_4(s)$)
- Solubility = 50.0 mg/L (45 °C)
- Micron-sized particles

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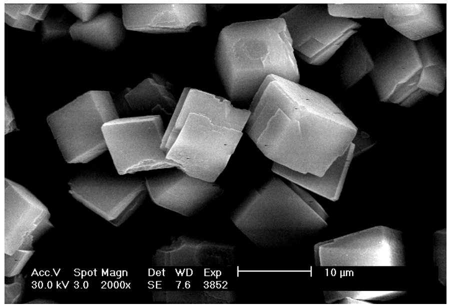
Crystallization and Precipitation - Examples

calcite $CaCO_3$

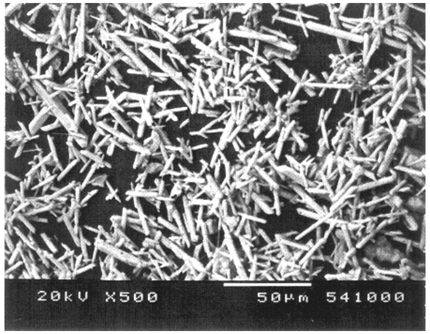
solubility = 13 mg / L



https://www.howitworksdaily.com/the-giant-crystal-cave/

gypsum $CaSO_4 \cdot 2H_2O$

solubility = 2600 mg/L



Illustrations from: https://www.howitworksdaily.com/the-giant-crystal-cave/
https://thecrystalcouncil.com/crystals/iceland-spar

Precipitation or crystallization!!

Crystallization → large crystals
Crystallization → slow process
Precipitation → small crystals
Precipitation → fast process
Large crystals → more soluble salts
Small crystals → less soluble salts

Precipitate → very often crystals!

Some definitions...

Precipitation = crystallization of slightly soluble salts
Precipitation = fast crystallization (high saturation!)

Crystallization ↔ soluble salts
Precipitation ↔ slightly soluble salts

PRECIPITATION → MORE GENERAL TERM

Solubility

Solubility (definition) = the maximum amount of substance that will dissolve in a given amount of solvent at certain temperature (concentration of substance in saturated solution, c_s)

Empirical classification of solubility of solids in water:

Insoluble	$c_s < 0.01$ mol/L
Slightly soluble	$0.01 < c_s < 0.1$ mol/L
Soluble	$c_s > 0.1$ mol/L

Empirical solubility rules (...)

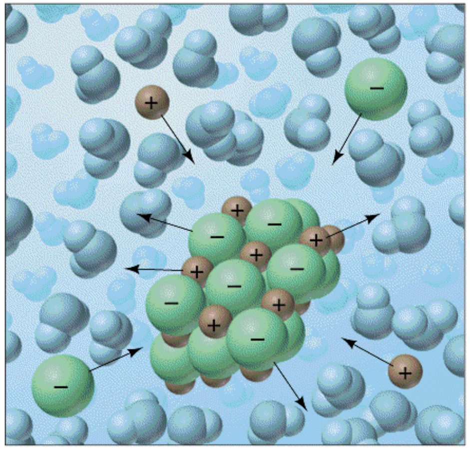
1. All sodium, potassium, and ammonium salts are soluble.
2. All nitrates, acetates and perchlorates are soluble.
3. All silver, lead and mercury(I) salts are insoluble.
4. All chlorides, bromides and iodides are soluble (!!!).
5. All carbonates, sulfides, oxides and hydroxides are insoluble (!!!).
6. All sulfates are soluble, except calcium sulfate and barium sulfate.

Equilibrium in systems of ionic salts (compound)

In saturated solution containing solid → dynamic equilibrium

$M_xA_Y \leftrightarrow xM^{m+} + yA^{a-}$

Dissolution rate of solid phase in excess = crystallization (precipitation) rate, $k_d = k_g$



Solubility product (K_{sp})

Equilibrium reactions	**Solubility product**
$CaCO_3(s) \leftrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$	$K_{sp} = [Ca^{2+}] \cdot [CO_3^{2-}]$
$AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$	$K_{sp} = [Ag^+] \cdot [Cl^-]$
$Al(OH)_3(s) \leftrightarrow Al^{3+}(aq) + 3OH^-(aq)$	$K_{sp} = [Al^{3+}] \cdot [OH^-]^3$
$Hg_2I_2(s) \leftrightarrow 2Hg^+(aq) + 2I^-(aq)$	$K_{sp} = [Hg^+]^2 \cdot [I^-]^2$
$CaF_2(s) \leftrightarrow Ca^{2+}(aq) + 2F^-(aq)$	$K_{sp} = [Ca^{2+}] \cdot [F^-]^2$

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Solubility product, K_{sp} → Estimate of solubility (c_s)

Calcium carbonate ($CaCO_3$)

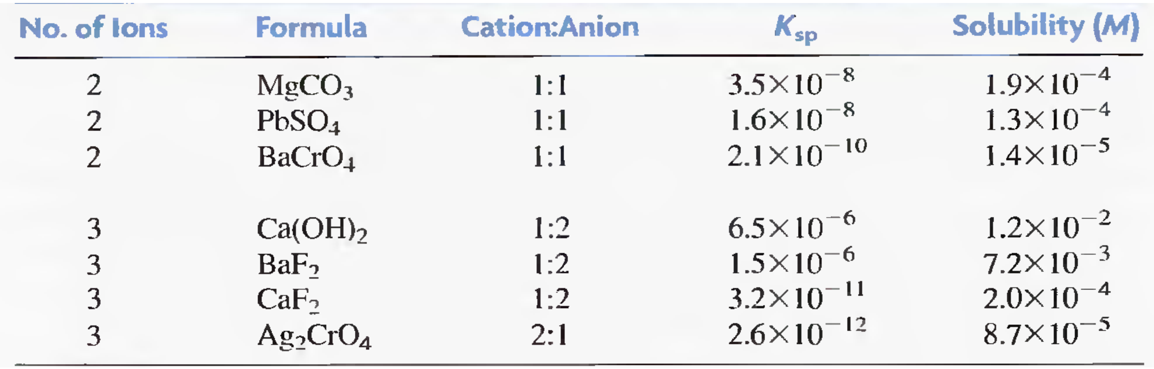
$$K_{sp} = [Ca^{2+}] \cdot [CO_3^{2-}]$$

$$c_s = [Ca^{2+}]_{eq} = [CO_3^{2-}]_{eq} = \sqrt[2]{[Ca^{2+}] \cdot [CO_3^{2-}]} = \sqrt[2]{K_{sp}}$$

Calcium fluoride (CaF_2)

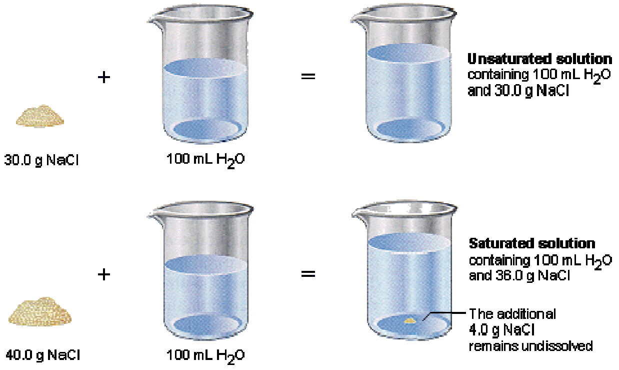
$$K_{sp} = [Ca^{2+}] \cdot [F^-]^2$$

$$c_s = [Ca^{2+}]_{eq} = \frac{1}{2}[F^-]_{eq} = \sqrt[3]{[Ca^{2+}] \cdot [F^-]^2} = \sqrt[3]{K_{sp}}$$



No. of Ions	Formula	Cation:Anion	K_{sp}	Solubility (*M*)
2	$MgCO_3$	1:1	3.5×10^{-8}	1.9×10^{-4}
2	$PbSO_4$	1:1	1.6×10^{-8}	1.3×10^{-4}
2	$BaCrO_4$	1:1	2.1×10^{-10}	1.4×10^{-5}
3	$Ca(OH)_2$	1:2	6.5×10^{-6}	1.2×10^{-2}
3	BaF_2	1:2	1.5×10^{-6}	7.2×10^{-3}
3	CaF_2	1:2	3.2×10^{-11}	2.0×10^{-4}
3	Ag_2CrO_4	2:1	2.6×10^{-12}	8.7×10^{-5}

Measure of solution stability



$c = c_s$	saturated solution (no dissolution, no precipitation → equilibrium)
$c < c_s$	undersaturated solution (dissolution of solid phase)
$c > c_s$	supersaturated solution (precipitation of solid phase)

Supersaturation definition

Precipitation affinity	$\phi = RT \ln (c / c_s)$
Saturation ratio	$S = \frac{c}{c_s}$
Absolute supersaturation	$c - c_s$
Relative supersaturation	$\frac{c - c_s}{c_s} \equiv S - 1$
Saturation index	$SI \equiv \log(\frac{c}{c_s})$

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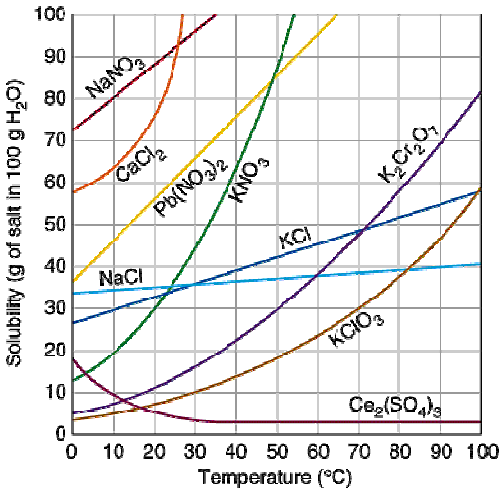
Factors which determine the solubility of ionic salts



Temperature change → Increase of solubility (!)

Complexation of constituent ions → Increase of solubility

$CaCO_3(s) \leftrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq) + (EDTA \rightarrow CaEDTA)$

Strong acid addition → Increase of solubility (salts of weak acids – carbonates, fluorides, phosphates…)

$CaCO_3(s) \leftrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq) + (H_3O^+ \rightarrow HCO_3^-)$

Common ion addition → Decrease of solubility

$CaCO_3(s) \leftrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq) + (CaCl_2(aq))$

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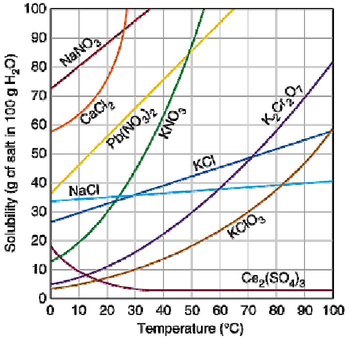
How to initiate precipitation / crystallization??



1. Temperature change

2. Evaporation of solvent – change of constituent ion concentration

3. Chemical reaction / mixing the components

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Chemical reaction (mixing the reactants) → suitable for slightly soluble salts

Soluble salt AX + Soluble salt BY → Insoluble salt AB + Soluble X + Soluble Y

$2\ AgNO_3 + K_2CrO_4 \leftrightharpoons Ag_2CrO_4(s) + 2\ KNO_3$

$2Ag^+ + 2NO_3^- + 2K^+ + CrO_4^{2-} \leftrightharpoons Ag_2CrO_4(s) + 2K^+ + 2NO_3^-$

$CaCl_2 + Na_2CO_3 \leftrightharpoons CaCO_3(s) + 2NaCl$

$Ca^{2+} + 2Cl^- + 2Na^+ + CO_3^{2-} \leftrightharpoons CaCO_3(s) + 2Na^+ + 2Cl^-$

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Importance of investigation of crystallization (precipitation)???

Geology, geochemistry, ocenology

- Formation of sedimentary rocks and minerals
- Sea water buffering: absorption of $CO_2 \rightarrow CaCO_3$ precipitation → global warming, acidification...

Technology (industrial crystallization)

- First technological process in history – alum production (tanning)
- 60 - 70 % product of basic chemical and pharmaceutical industry – by precipitation
- Unwanted precipitation – incrustation, limescale...

Biomedicine, biology

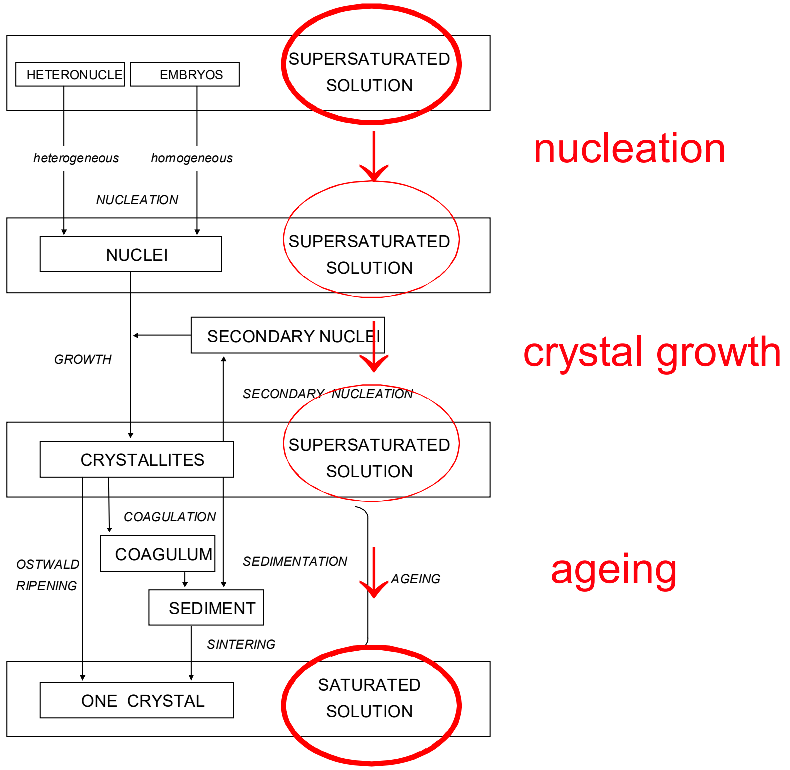
- Biomineralization, pathological mineralization (bones, teeth, shells, ...) → materials science

Environmental protection....

Mechanisms of precipitation (crystallization) processes

(Physical-chemical process of formation of new phase in homogeneous system)

Precipitation → Stepwise process = Nucleation + Crystal Growth + Ageing



HETERONUCLEI

EMBRYOS

SUPERSATURATED SOLUTION

heterogeneous

homogeneous

NUCLEATION

nucleation

NUCLEI

SUPERSATURATED SOLUTION

SECONDARY NUCLEI

GROWTH

crystal growth

SECONDARY NUCLEATION

CRYSTALLITES

SUPERSATURATED SOLUTION

COAGULATION

COAGULUM

OSTWALD RIPENING

SEDIMENTATION

AGEING

ageing

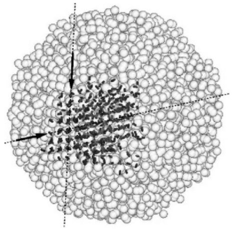
SEDIMENT

SINTERING

ONE CRYSTAL

SATURATED SOLUTION

Nucleation



Initial formation of new phase in homogeneous solution – energetically most demanding

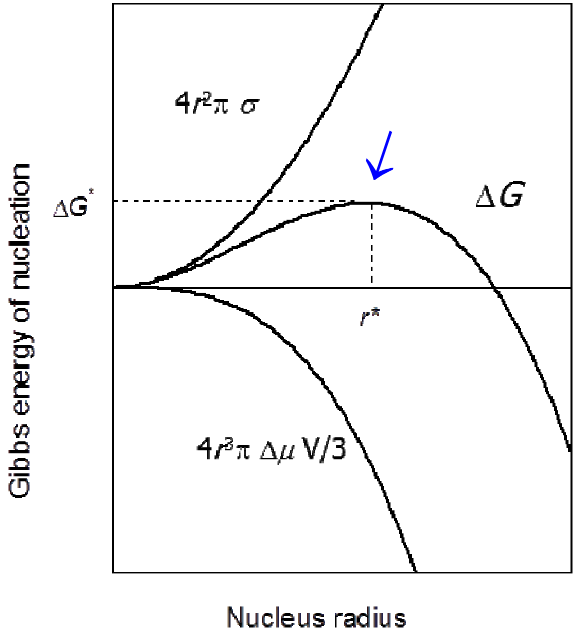
Classical nucleation theory: Nucleus (r*) is a tiny peace of solid phase with all physical chemical properties of macroscopic structure, which stabilize by dissolution or growth

Dimensions – several constituting units (ions, molecules...)

Unstable – dissolution or growth of critical nucleus

Unpredictable in volume of solution

No direct observation of nucleation (Instead, from chemical and mineralogical composition, number and size of crystals)



Macroscopic parameters (V, A, σ, μ)

$$\Delta G = \Delta G_{Vol} + \Delta G_{Sur}$$

$$\Delta G = V\,\Delta\mu_v + A\,\sigma$$

$$\Delta G = (4r^3\pi/3)\,\Delta\mu_v + 4r^2\pi\ \sigma$$

Number of nuclei (crystals) vs. initial supersaturation

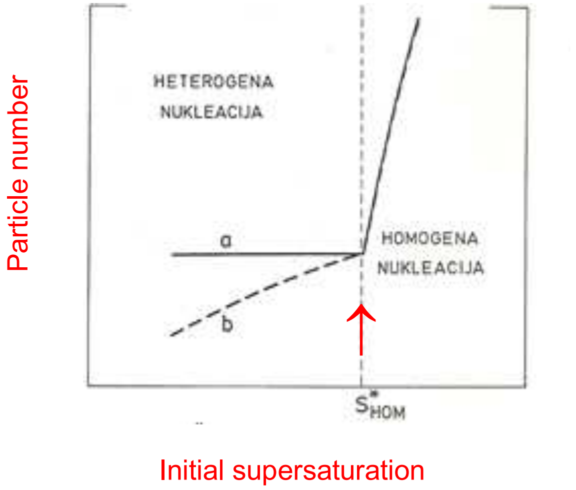
(a) Homogeneous nucleation - by interaction (collision) of constituents

$n \approx 10^7 - 10^{12}\ \mathrm{cm}^{-3}$

(b) Heterogeneous nucleation – catalyzed by suspended impurities, seeding

$n \approx 10^6 - 10^7\ \mathrm{cm}^{-3}$

(Water undercooling: - 48.3 °C)



Nucleation rate

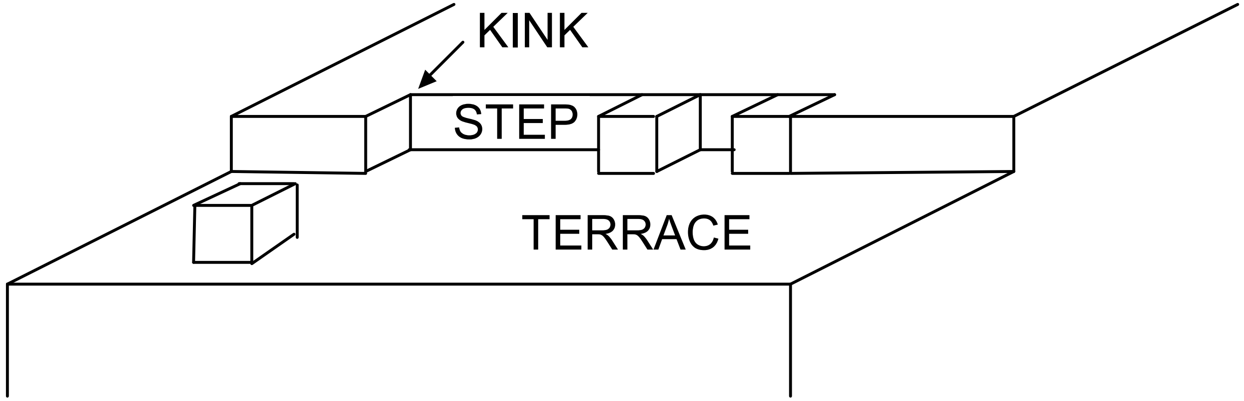
$$J = B \cdot \exp(-C / \ln^2 S)$$

S^*_{HOM} – critical supersaturation for homogeneous nucleation

Crystal growth

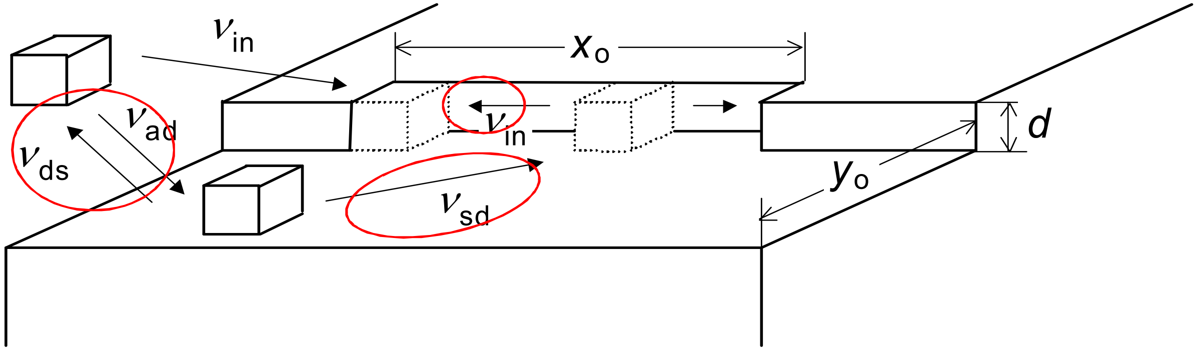
Continuous incorporation of constituent units into crystals which is in contact with supersaturated solution

Incorporation into energetically favored position at surfaces (kinks, steps)



Crystal growth = consecutive processes → slowest process control the overall growth

Volume diffusion and convection of growth units
Adsorption
Surface diffusion
Edge diffusion

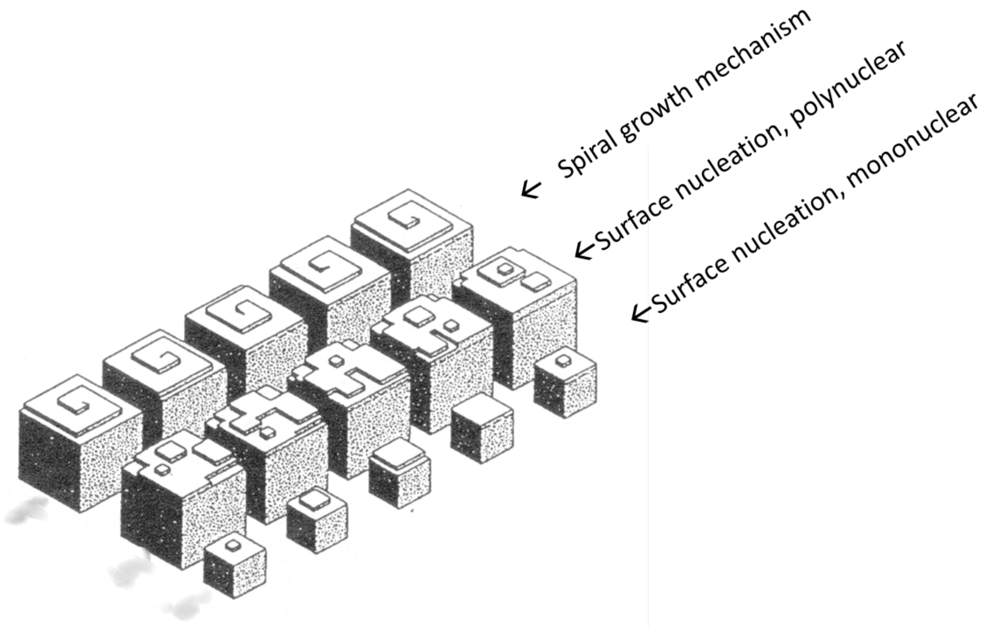


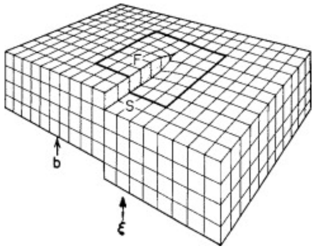
1. Transport controlled mechanisms

Diffusion controlled growth	$rate = D \cdot V_m \cdot (c-c_s)/r$	$\approx K_d \cdot (c-c_s)/r$	"Linear growth rate low"
Adsorption controlled growth	$rate = (V_m/A)Ad(c\nu_{ad} - AdK_{ad}c_s\nu_{ds}) = V_m d\nu_{ad}c_s(S-1)$	$\approx k_1(S-1)$	"Linear growth rate low"

2. Surface controlled mechanisms (incorporation of constituents into crystal structure)

Surface nucleation controlled growth	$rate = A \cdot \exp(-B/\ln S)$	"Exponential growth rate low"
Spiral (dislocation) controlled growth	$rate = k_2 \cdot (S-1) \cdot \ln S \quad \approx k_2 \cdot (S-1)^2$	"Parabolic growth rate low"

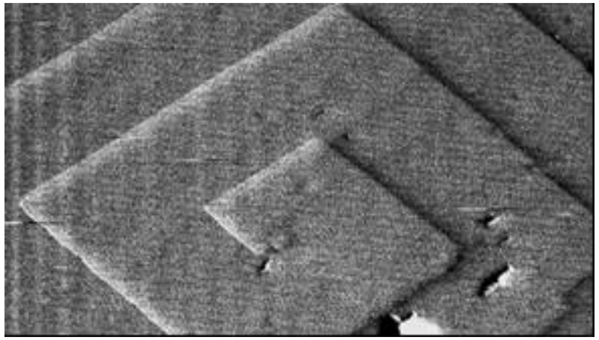




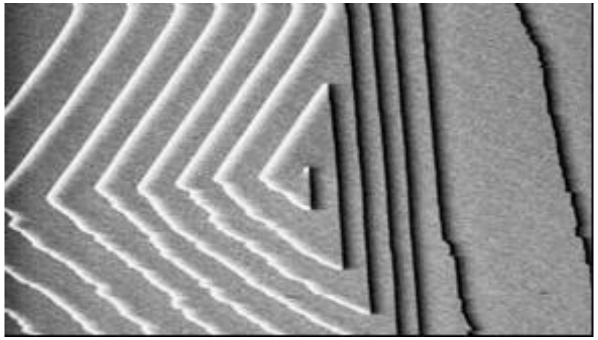
Visualization of crystal surfaces during growth in solution

Atomic force microscopy (AFM)

Growth on spiral step

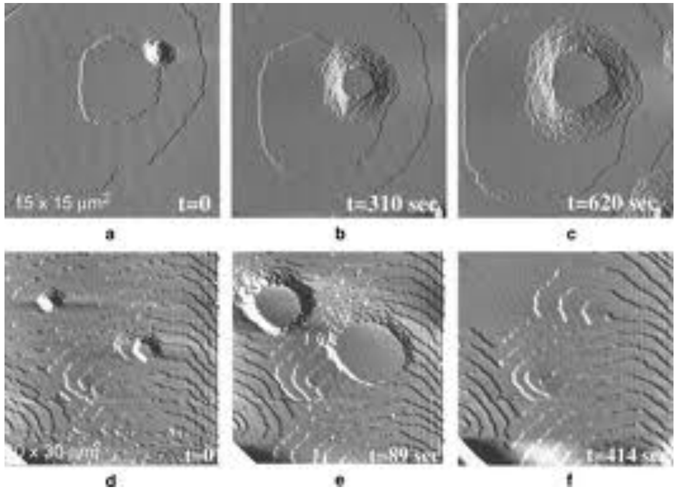


Calcite ($CaCO_3$)

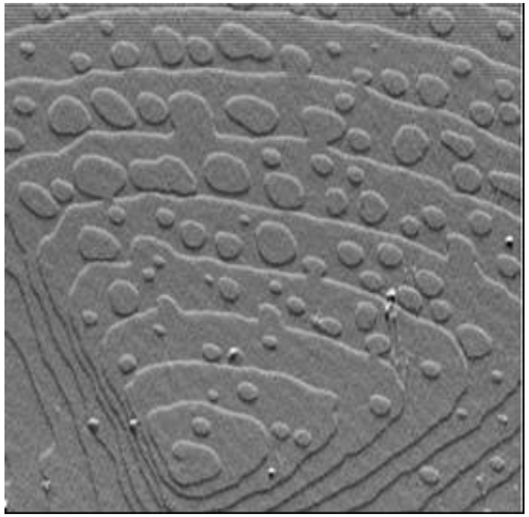


Brushite ($CaHPO_4 \cdot 2H_2O$)

Surface nucleation)



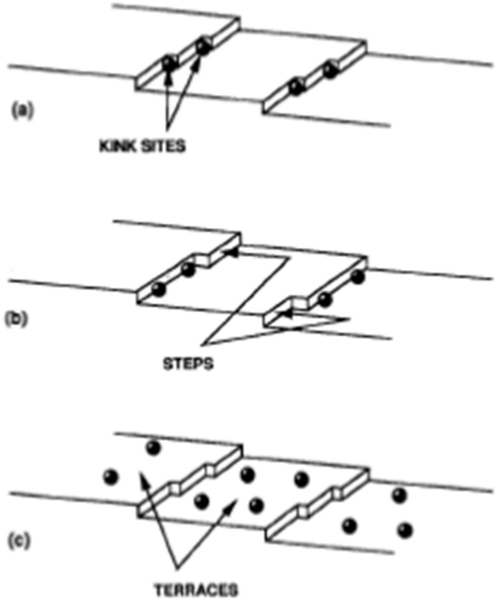
Growth on spiral step + surface nucleation



Impurities and crystal growth

Impurity - any foreign substance other than precipitating (crystallizing) compound

Additive - deliberately added impurity



Impurities in contact with crystallizing compound adsorb on surfaces
at the terraces (immobile additives)
at position on growing steps (mobile additives)

Decrease the growth rate – adsorbed at active sites on the surface or in the kink, impede the step propagation

Occasionally: increase the growth rate – incorporation into structure - changing the crystal properties (interfacial energy)

Change the crystal morphology !!!!

Change the growth mechanism!!!!

Why to investigate crystal growth kinetics and mechanisms??

1. Precipitation kinetics (kinetic data)

↓

2. Precipitation mechanisms

Precipitation mechanisms ??

Described by **kinetic laws** – correlate the growth rate and respective supersaturation

Growth rate = Constant × Function of supersaturation

$$rate = -\mathrm{d}c/\mathrm{d}t = k_r \times (c - c_s)^n$$

(analysis of kinetic data: testing and comparison of theoretical growth models (mechanisms) with experimental data)

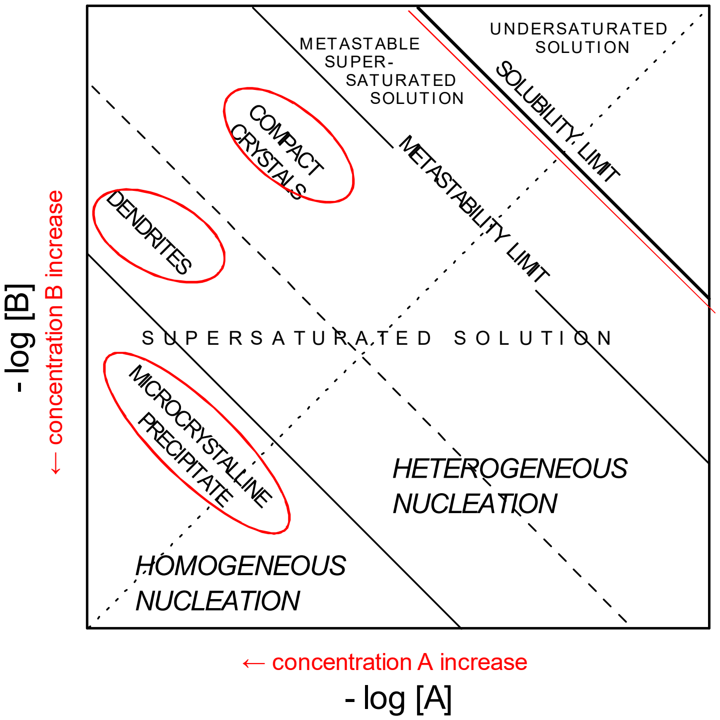
↓

3. Control of physical / chemical properties of precipitate

Research Strategy

A. Precipitation diagrams

- Graphical presentation of precipitation system (screening)
- Experimentally obtained properties shown as a function of concentration of reactants, sampled at identical experimental conditions (time, pH, temperature, mode of mixing, additives...)
  - mineralogical (chemical) composition of precipitate
  - morphology
  - size distribution



- Isergones - lines of constant relative supersaturation (S-1)
- Solubility boundary, (S-1) = 0
- Precipitation boundary (metastability limit), (S-1) > 0
- Homogeneous nucleation (precipitation) (S-1) >> 0

Critical precipitation parameters
vs.
Critical properties of solid phase

Supersaturation (initial concentration of reactants)

Temperature

Constituent ions ratio

Presence of additives / impurities

Hydrodynamics

vs.

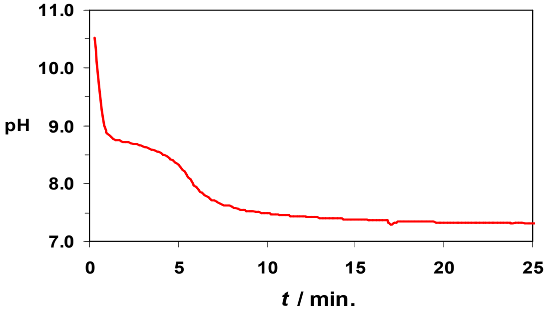
Size distribution

Morphology

Polymorphism / chemical composition

B. Precipitation kinetics and mechanism

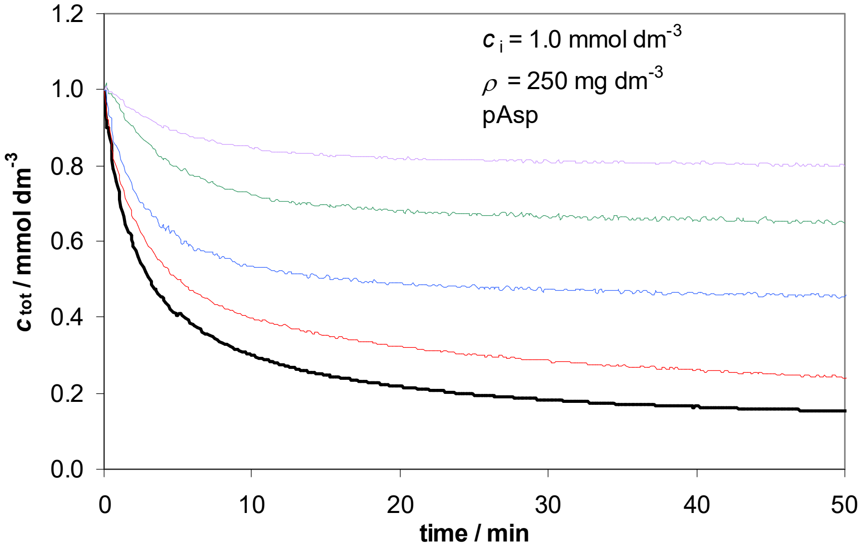
Data acquisition



Experimental set-up – measurements of reaction propagation
Beaker + Temperature control + Stirring
Sensor - progress of reaction (ion selective electrode, pH, conductivity, size distribution, chemical analysis...)

Analysis of growth kinetics

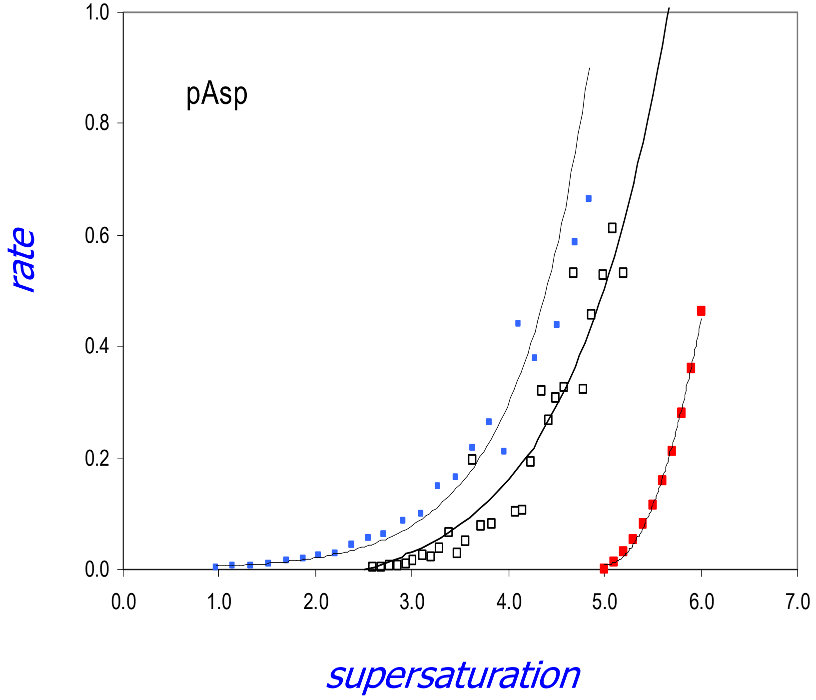
1. Progress curves



$c = \mathrm{f}\ (t)$

↓

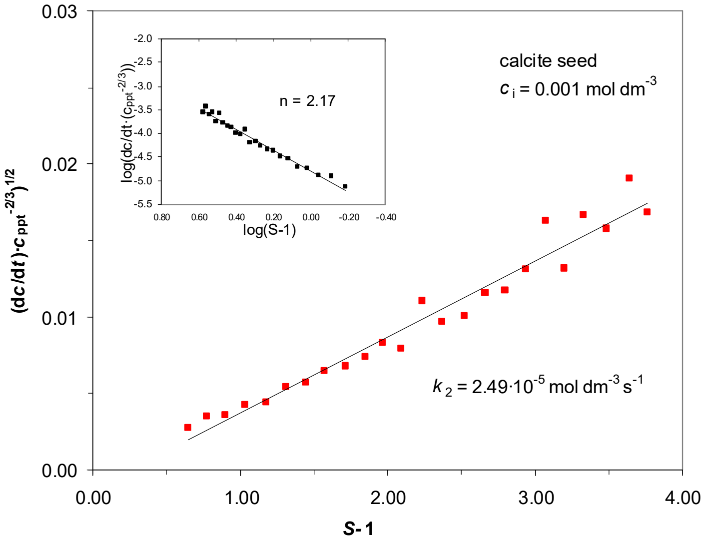
2. Calculation of growth rate and supersaturation

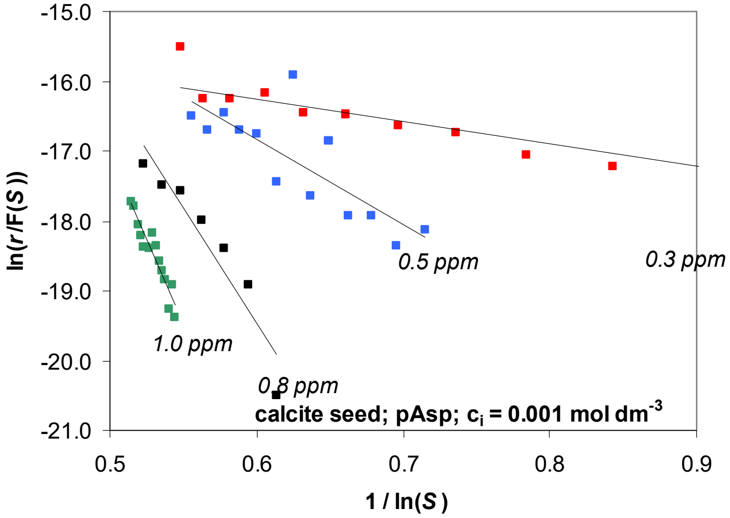


$$rate = \mathrm{f}\ (c\text{-}c_s)$$

↓

3. Testing the theoretical crystal growth laws (models)





$$v = k_2\,(S - 1)^2$$

$$\ln(v) = k_e \cdot (1/\ln S)$$

Parabolic growth rate → Growth on dislocation

Exponential growth rate → Nucleation control

↓

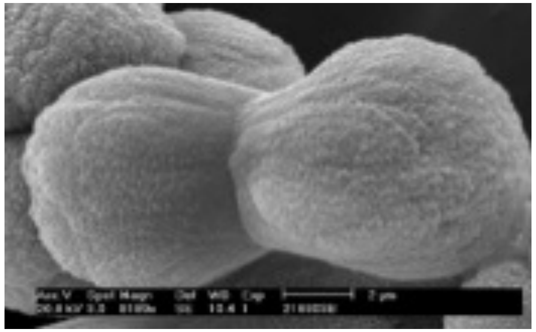
4. Analytical characterization of solution and solid phase

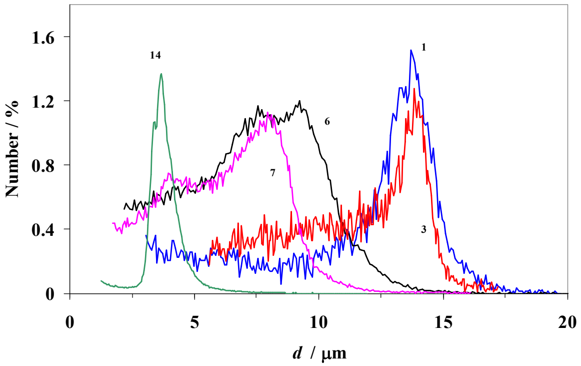
Morphology (SEM / EDX)

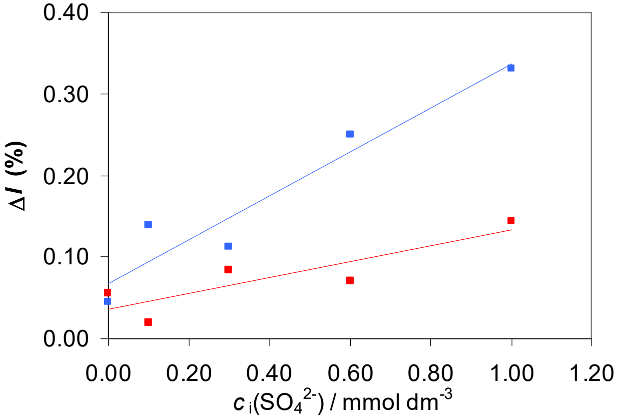
Crystal size distribution (DLS, CC)

Chemical analysis (chromatography, spectroscopy...)

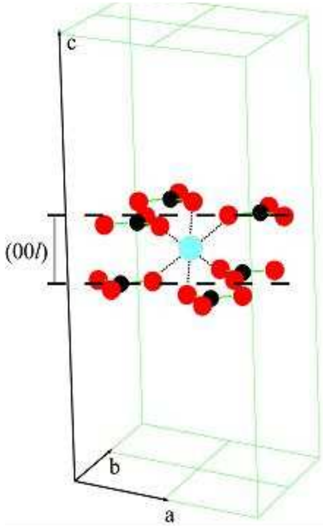
Structural analyses (FTIR, PXRD, EPR, ss-NMR...)

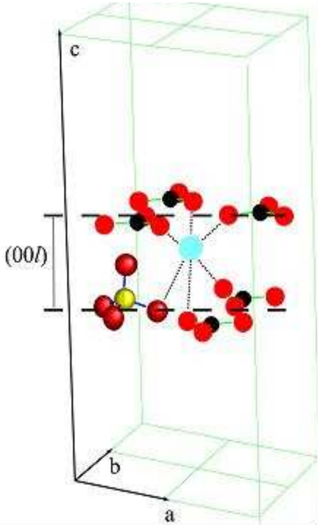






5. Results - models





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Crystallization in Environment and Environmental Protection

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2. Calcium Carbonate Precipitation

Calcium carbonate: “ordinary” material

Geological $CaCO_3$


Karst / limestone


Tufa


Travertine


Chalk


Stalactite, stalagmite

Biominerals

Limescale

Properties	
Molecular formula	$CaCO_3$
Exact mass	100.0869 g/mol
Appearance	Fine white powder
Density	2.71 g/cm^3 (calcite) 2.83 g/cm^3 (aragonite) ?????
Melting point	825 °C (aragonite) 1339 °C (calcite)
Boiling point	decomposes
Solubility in water	0.00015 mol/L (25°C)
Solubility product, K_{sp}	4.810^{-9} ?????
Solubility in dilute acids	soluble
Acidity (pK_a)	9.0
Refractive index (n_D)	1.59
Structure	
Crystal structure	Trigonal
Space group	2/m

http://en.wikipedia.org/wiki/Calcium_carbonate)

Calcite – Iceland spar

aragonite

marble

travertine, tufa

CALCIUM CARBONATE PHASES AT ENVIRONMENTAL CONDITIONS

AMORPHOUS

AMORPHOUS CALCIUM CARBONATE	$CaCO_3 \cdot nH_2O$

HYDRATES

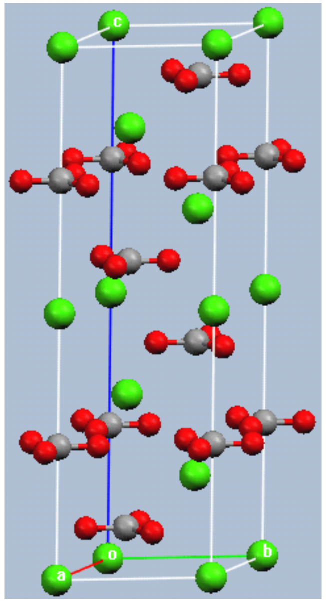
CALCIUM CARBONATE HEKSAHYDRATE ()	$CaCO_3 \cdot 6H_2O$
CALCIUM CARBONATE MONOHYDRATE (IKAITE)	$CaCO_3 \cdot H_2O$

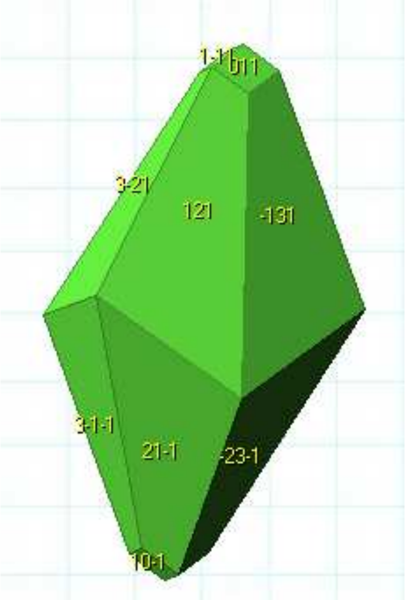
POLYMORPHS

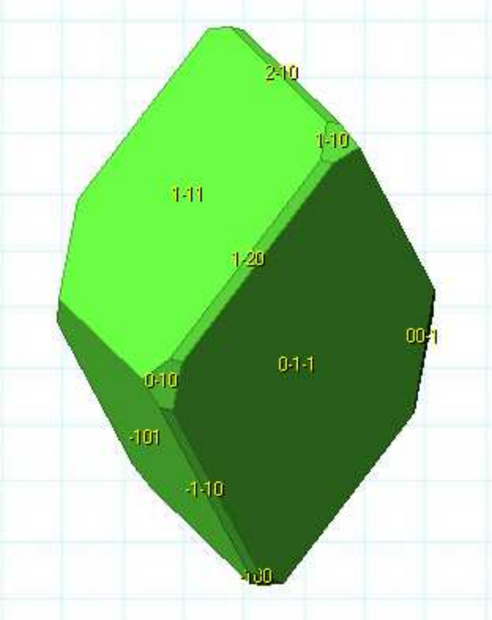
VATERIT	$CaCO_3$
ARAGONIT	$CaCO_3$
KALCIT	$CaCO_3$

CALCITE

Most stable polymorph
Wide spread mineral (≈ 4 % Earth crust)
Formation at different periods of Earth history
More than 800 crystal forms
Trigonal crystal system, hexagonal lattice system, Ca coordinated with 6 CO_3^{2-}
Unit cell: a = 4.9896(2) Å, c = 17.0610(11) Å;







http://en.wikipedia.org/wiki/Calcium_carbonate)

Typical crystal habit

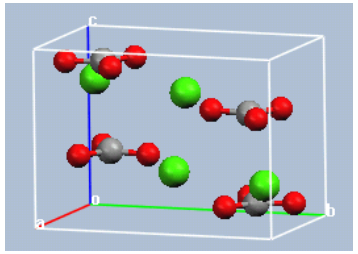
scalenohedral

microcrystalline aggregate

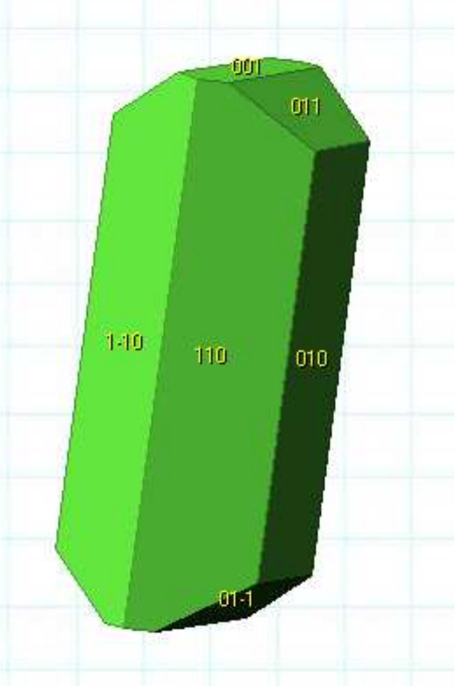
rhombohedral

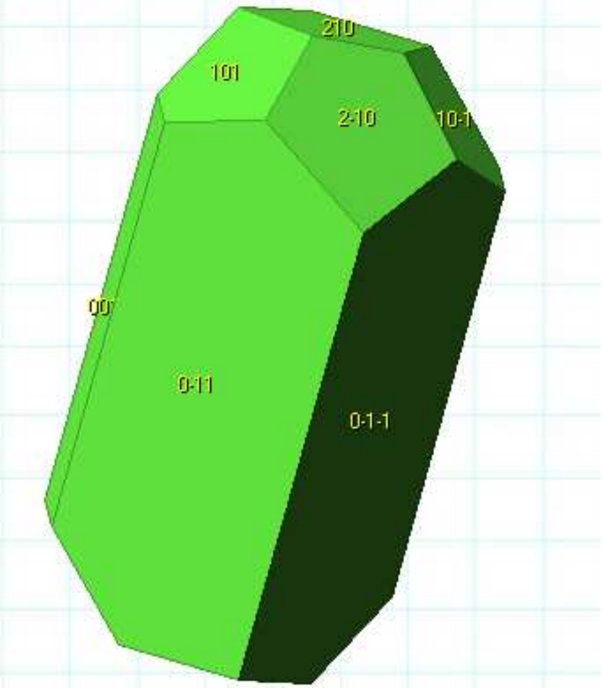
ARAGONITE

Less stable modification (high pressure, high temperature modification)
Formation in presence of Mg^{2+}
Slow transformation of geological deposits to calcite (10 to 100 M years)
Important biomineral – corals, mollusk shell (nacreous layer or entire) ...
Orthorhombic crystal system, dipyramidal crystal class, Ca coordinated with 9 CO_3^{2-}
Unit cell: a = 4.95 Å, b = 7.96 Å, c = 5.74 Å;



http://en.wikipedia.org/wiki/Calcium_carbonate)



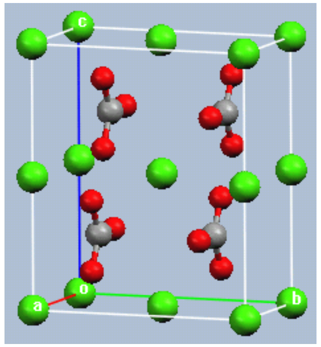


Typical crystal habit

Prismatic, acicular, columnar, globular

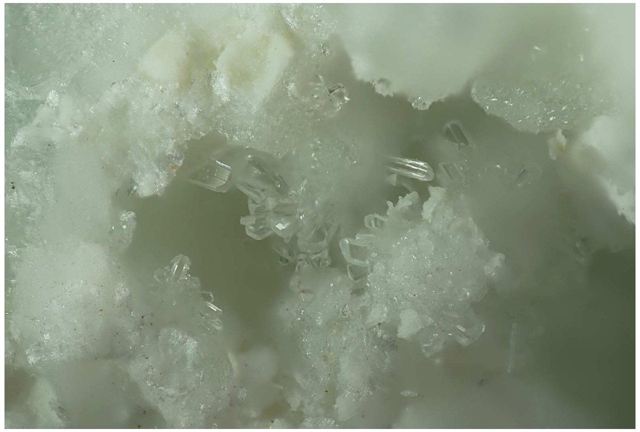
VATERITE

Least stable $CaCO_3$ polymorph
Uncommon in nature (fast transformation in aqueous environment)
Stabilized by organic macromolecules – biomineralization (fish otoliths), pathological mineralization (gallstone)
Hexagonal crystal system; dihexagonal dipyramidal crystal class, Ca coordinated with 8 CO_3^{2-}
Unit cell: a = 4.13 Å, c = 8.49 Å



http://en.wikipedia.org/wiki/Calcium_carbonate)

VATERITE



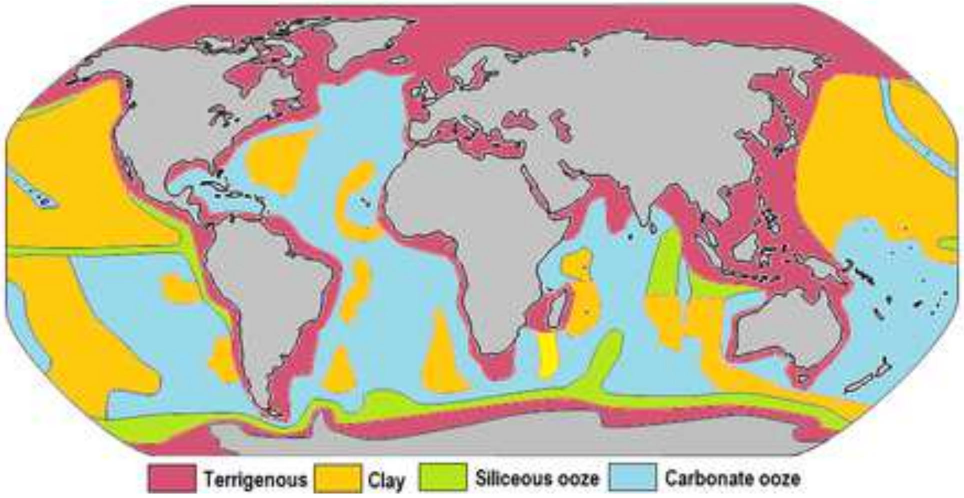
Calcium carbonate: “Extraordinary mineral”??

(Do you know that...)

… $CaCO_3$ is one of the most abundant mineral ...

4% Earth crust, 20% sedimentary rocks – chalk, limestone, tufa, travertine ...

25% seafloor sediment – containing more than 30% $CaCO_3$

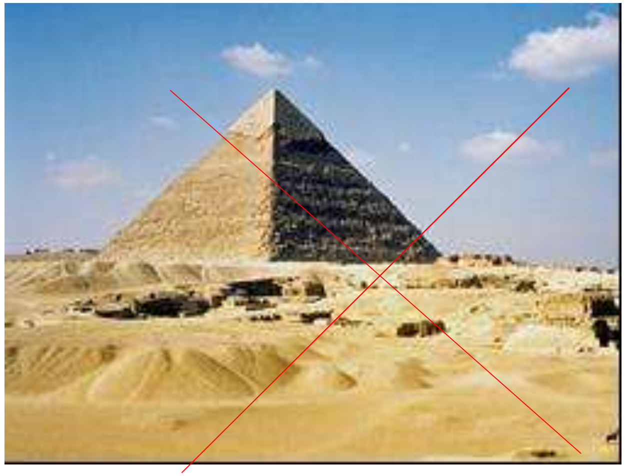


http://en.wikipedia.org/wiki/

… the tallest man-made structure is made of calcium carbonate (limestone)

Great pyramid (Pyramid of Khufu) (2550 – 2500 p.n.e)

Tura - the finest and whitest limestone of all Egyptian quarries



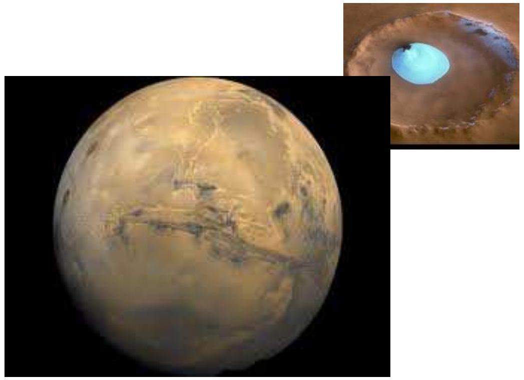
~~Khafre pyramid → granite + limestone~~

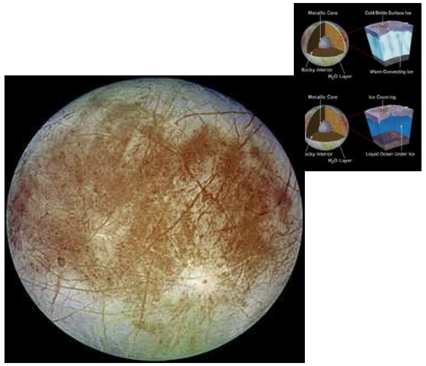
… the calcium carbonate is found only on Earth…

only in aqueous solution:

$\mathrm{Ca^{2+}}(aq) + \mathrm{CO_3^{2-}}(aq) \leftrightarrow \mathrm{CaCO_3}\ (s)$

What about Mars, Europa, ... ??





$CaCO_3$ and search for extraterrestrial life

SNC (Martian) meteorites (Shergottites, Nakhlites, Chassignites)

Elemental and isotopic compositions similar to Mars' rocks and atmosphere

Shergotty meteorite

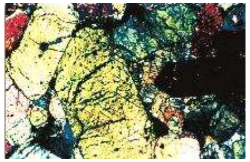
Shergotty, Bihar, India (1865)

Nakhla meteorite

Nakhla, Aleksandria, Egipat (1911)

Chassigny meteorite

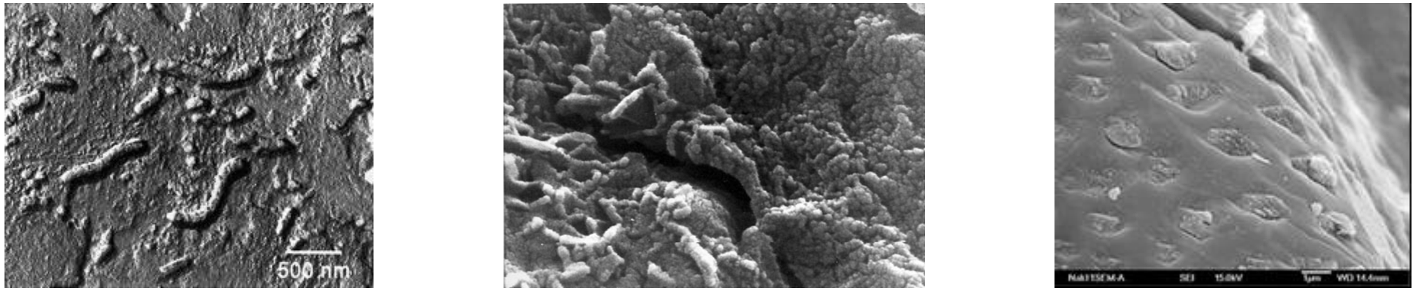
Chassigny, Francuska (1815)



http://en.wikipedia.org/wiki/

ALH 84001 meteorite

Allan Hills, Antarctica (1984)



David S. McKay et al.: Search for Past Life on Mars: Possible Relic Biogenic Activity in Martian Meteorite ALH84001

Science, 1996, Vol. 273 no. 5277 pp. 924-930

Calcium carbonate in seawater and oceans

Origin of seawater and oceans

Water: Volcanoes – degassing from molten rocks (and/ or comets)

Minerals

Majority of minerals → rainfall washout of the ground (continental weathering)

Na^+ → additionally leached out from ocean floor

Cl^-, SO_4^{2-} HCO_3^-, ... → outgassing from Earth interior (volcanos, hydrothermal vents)

Salinity → stable during the Earth's history

Ca^{2+}/ Mg^{2+} → variable during the Earth's history

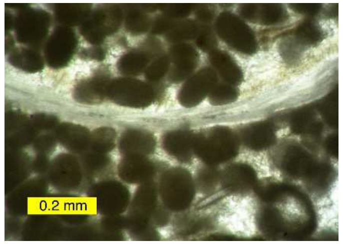
http://en.wikipedia.org/wiki/

$CaCO_3$ precipitation - inorganic

Dominant during the early time of Earth history (Precambrian) (+ microorganisms - stromatolites)

Modern seawater - supersaturated with respect to $CaCO_3$

Ooids, peloids



$CaCO_3$ precipitation – biological

Dominant during the Phanerozoic (last 540 million years of the Earth's history)

Mineralogical composition

- Low-magnesium calcite (brachiopods, planktonic foraminifera, coccoliths)
- High-magnesium calcite (benthic foraminifera, echinoderms, coralline algae)
- Aragonite (mollusks, calcareous green algae, stromatoporoids, corals, tube worms)

http://en.wikipedia.org/wiki/

$CaCO_3$ precipitation during the Earth's history

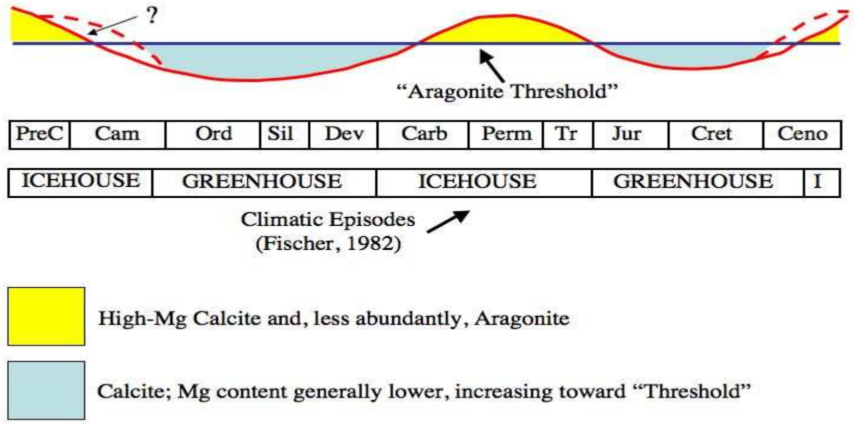
Calcite sea

Low magnesium calcite dominant inorganic $CaCO_3$ precipitate

Formation of carbonate hardground, calcitic ooids, calcite cements, dissolution of aragonite shell

Aragonite sea

Aragonite and high-magnesium calcite dominant inorganic $CaCO_3$ precipitate



After Sandberg (1983)

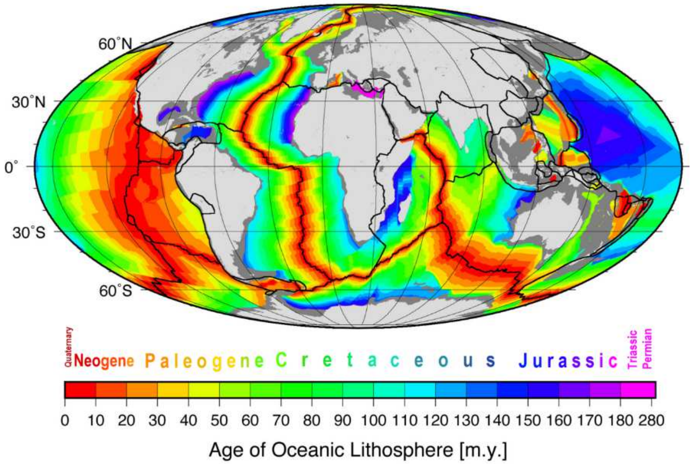
Why calcite sea?

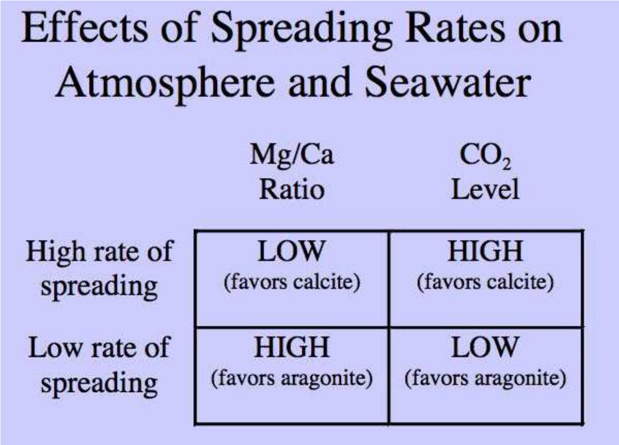
Rapid seafloor spreading at mid-ocean ridges

- seawater cycling through hydrothermal vents
- reduction of Mg by metamorphosis
- (Ca-rich minerals → Mg-rich basalt or clays (hydrothermal alteration))

Global greenhouse conditions

- volcanism → high CO_2 content favor calcite formation





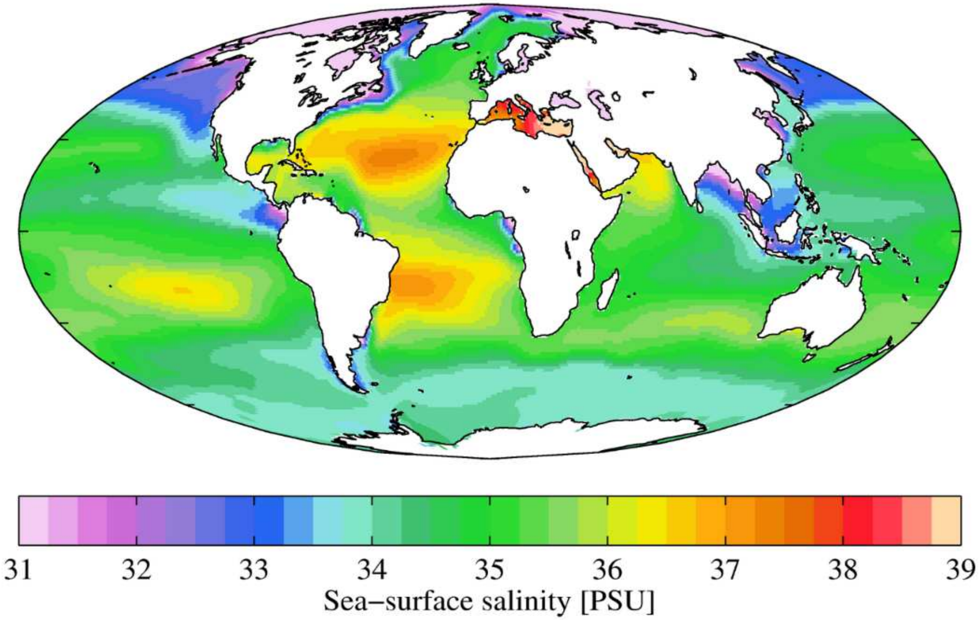
Effects of Spreading Rates on Atmosphere and Seawater

	Mg/Ca Ratio	CO_2 Level
High rate of spreading	LOW (favors calcite)	HIGH (favors calcite)
Low rate of spreading	HIGH (favors aragonite)	LOW (favors aragonite)

http://en.wikipedia.org/wiki/

Composition of modern (aragonitic!) seawater

Salinity = quantity of dissolved salts in water



pH = 7.5 - 8.4

http://en.wikipedia.org/wiki/

Chemical composition (average)

(35 ‰ salinity)

Component	Concentration (mol/kg)
Cl^-	0.546
Na^+	0.469
Mg^{2+}	0.0528
SO_4^{2-}	0.0282
Ca^{2+}	0.0103
K^+	0.0102
HCO_3^-	0.00206
Br^-	0.000844
$B(OH)_3$	0.000416
Sr^{2+}	0.000091
F^-	0.000068

Protocol for artificial seawater (ASW) preparation

(35 ‰ salinity)

"Gravimetric" salts

Salt	g kg^{-1} solution
Sodium chloride (NaCl)	23.926
Sodium sulfate (Na_2SO_4)	4.008
Potassium chloride (KCl)	0.677
Sodium bicarbonate ($NaHCO_3$)	0.196
Potassium bromide (KBr)	0.098
Boric acid (H_3BO_3)	0.026
Sodium fluoride (NaF)	0.003

"Volumetric" salts

Salt	mol kg^{-1} solution
Magnesium chloride ($MgCl_2.6H_2O$)	0.05327
Calcium chloride ($CaCl_2.2H_2O$)	0.01033
Strontium chloride ($SrCl_2.6H_2O$)	0.00009

Component	Seawater (mol/kg)	ASW (mol/kg)
Cl^-	0.546	0.54587
Na^+	0.469	0.46825
Mg^{2+}	0.0528	0.05327
SO_4^{2-}	0.0282	0.02822
Ca^{2+}	0.0103	0.01033
K^+	0.0102	0.00990
HCO_3^-	0.00206	0.00233
Br^-	0.000844	0.00082
$B(OH)_3$	0.000416	0.00042
Sr^{2+}	0.000091	0.00009
F^-	0.000068	0.00007

Seawater as precipitation system (major components)

Relevant ionic species

H^+, OH^-, Ca^{2+}, $CaCO_3^0$, $CaHCO_3^+$, $CaCl^+$, $CaSO_4^0$, $H_2CO_3^*$, HCO_3^-, CO_3^{2-},

Mg^{2+}, $MgCO_3^0$, $MgHCO_3^+$, $MgSO_4^0$, SO_4^{2-}, Cl^-, NO_3^-, Na^+, $NaCO_3^-$, K^+...

Mass balances

$$\mathbf{[Ca]_{tot}} = [Ca^{2+}]+[CaCO_3^0]+[CaHCO_3^+]+[CaSO_4^0]+[CaCl^+]$$

$$\mathbf{[CO_3]_{tot}} = [H_2CO_3^*]+[HCO_3^-]+[CO_3^{2-}]+[CaCO_3^0]+[CaHCO_3^+]+[MgCO_3^0]+[MgHCO_3^+]+[NaCO_3^-]$$

$$\mathbf{[Mg]_{tot}} = [Mg^{2+}]+[MgCO_3^0]+[MgHCO_3^+]+[MgSO_4^0]$$

Ionic equilibria

$$H_2CO_3^*(aq) \leftrightarrow 2\ H_2O + 2\ CO_2\ (g)$$

$$3\ CaCO_3(s) + 3\ H^+ \leftrightarrow 3\ Ca^{2+} + HCO_3^- + CO_3^{2-} + H_2CO_3^*$$

$$Ca^{2+} + HCO_3^- \leftrightarrow CaHCO_3^+$$

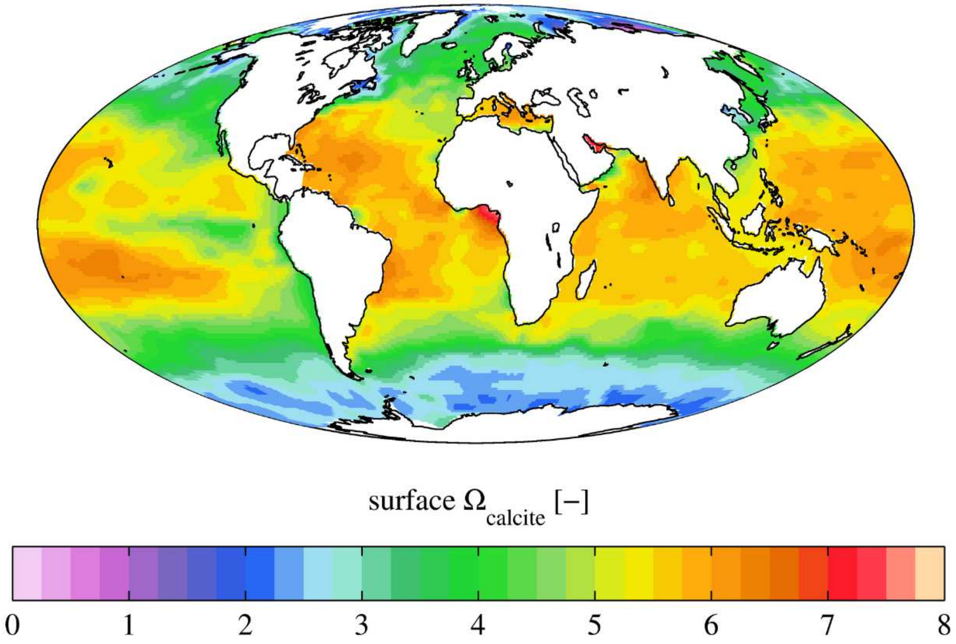
$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3^0$$

....

Calcium carbonate equilibrium in seawater

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \leftrightarrow CaCO_3(s)$$

$$\Omega = \frac{[Ca^{2+}]\cdot[CO_3^{2-}]}{K_{sp}}$$



http://en.wikipedia.org/wiki/

Vertical distribution of $CaCO_3$ saturation (Ω)

Shallow water - supersaturated with respect to $CaCO_3$ polymorphs (calcite, aragonite, vaterite)

- $CaCO_3$ shells of dead marine organisms preserved in the water column
- No significant spontaneous precipitation of $CaCO_3$ (!!!!)
  - High Mg^{2+} concentration - inhibition of calcite nucleation (precipitation)
  - Organic phosphate – inhibition of aragonite nucleation (precipitation)

Deep waters - undersaturated with respect to $CaCO_3$ polymorphs (calcite, aragonite, vaterite)

- Solubility increases with increasing pressure and salinity, decrease with temperature
- Dissolution of calcitic and aragonitic shells

Mid-depth zone: 0 - 3.5 km → sediment contains 85-95% $CaCO_3$

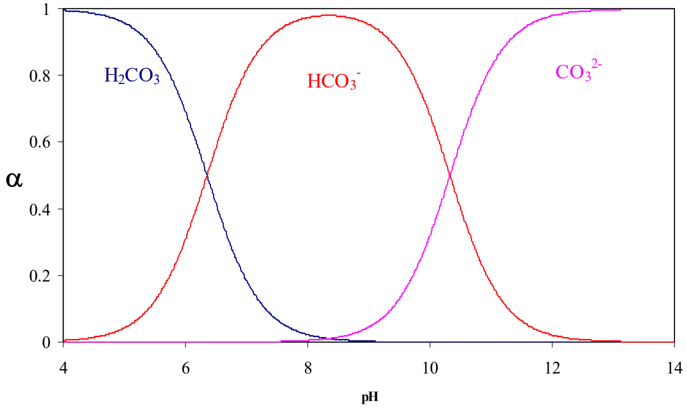
Transition zone: few hundred meters below 3.5 km → $CaCO_3$ content drop to around 10%

Abyssal depth → 0% $CaCO_3$

Lysocline = depth in the ocean below which the rate of dissolution of calcite increases dramatically ($d \approx 3.5$ km)

Calcite compensation depth = depth at which calcite deposition is completely compensated with dissolution

Role of calcium Carbonate in seawater



Precipitation / dissolution → major buffering mechanism in seawater

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \leftrightarrow CaCO_3(s)$$

$$H_2CO_3^0(aq) \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + H^+$$

Regulation of intensity of CO_2 exchange at the interface water / atmosphere

Global warming and seawater acidification by CO_2

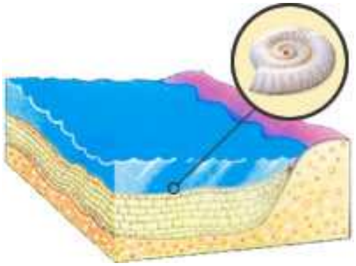
$\mathbf{p_{CO2}= 3{,}30 \cdot 10^{-4}}$ **atm** → pH = 8,21 → supersaturated (**calcite, aragonite**)

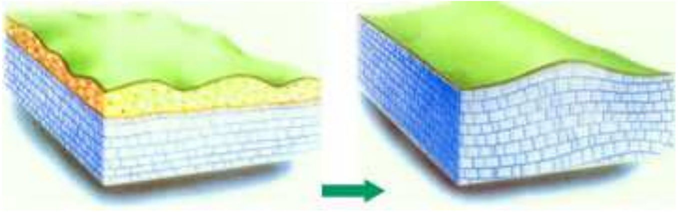
$\mathbf{p_{CO2}= 6{,}60 \cdot 10^{-4}}$ **atm** → pH = 7,96 → supersaturated (**calcite, aragonite**)

$\mathbf{p_{CO2}= 1{,}65 \cdot 10^{-3}}$ **atm** → pH = 7,61 → supersaturated (**calcite**), saturated (aragonite)

Calcium carbonate on mainland and karst topography

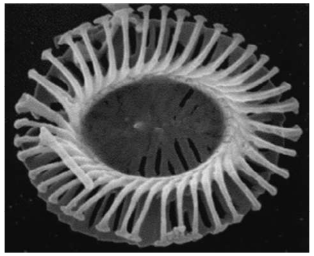
Diagenesis of seawater sediments

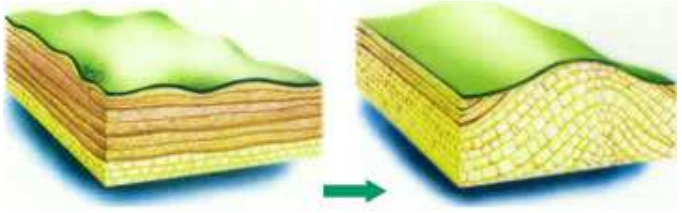




Chalk, 70 – 120 M years

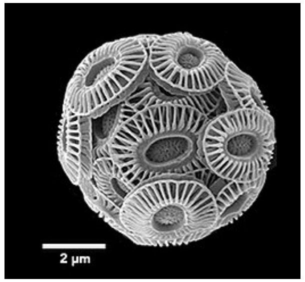
Planktonic or benthic protista (Foraminifera)

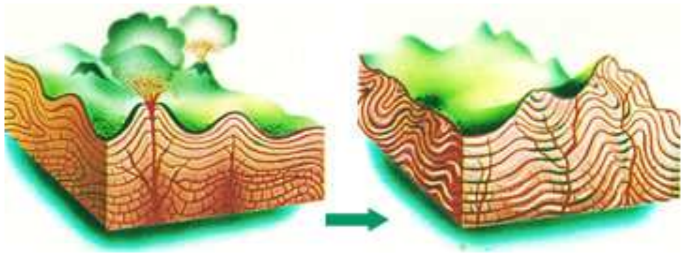




Limestone, 340 M years

Phytoplankton (coccolithophores (algae))



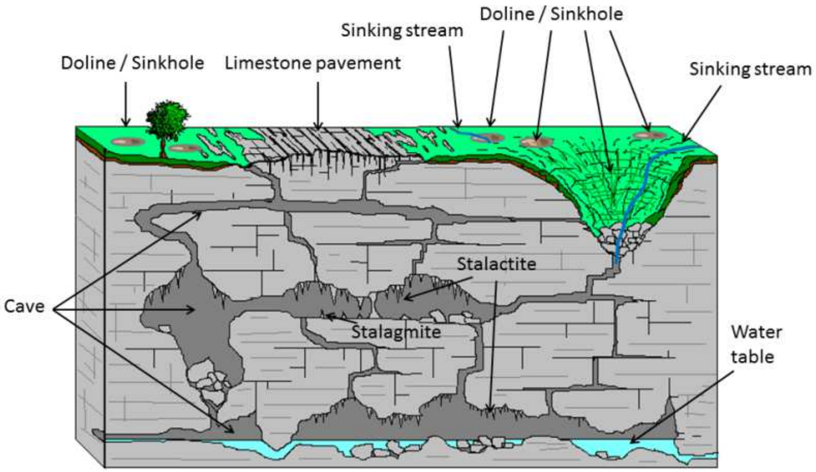


Marble = metamorphic limestone or chalk

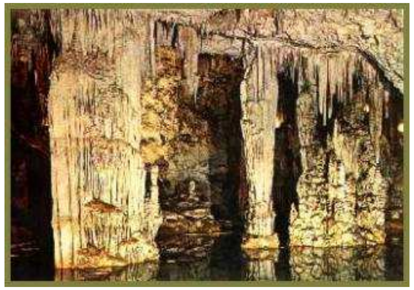
http://en.wikipedia.org/wiki/

Calcium carbonate on mainland and karst topography

Karst landscape → Earth's surface erosion of dense carbonate rock (limestone (calcite, aragonite) or dolomite)

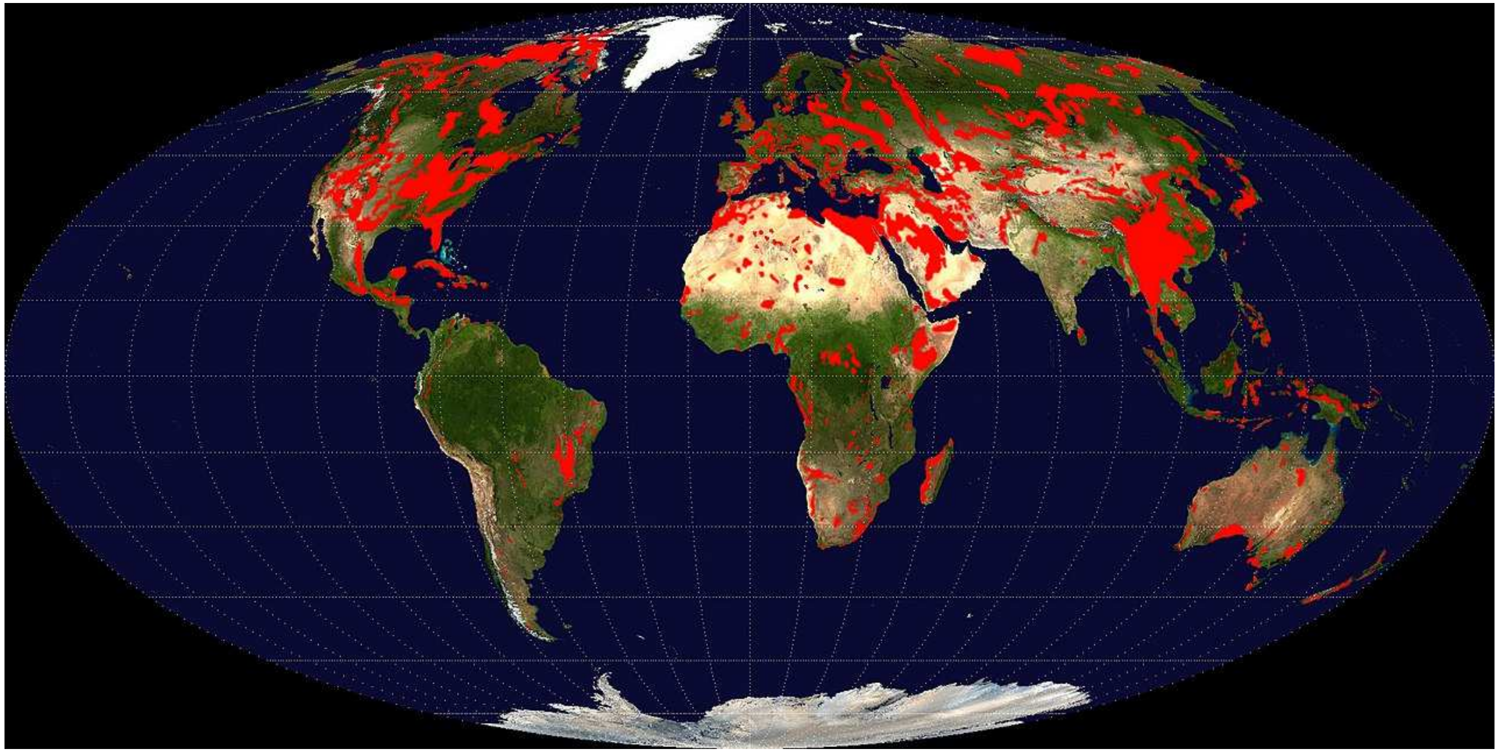


Typical karst landforms



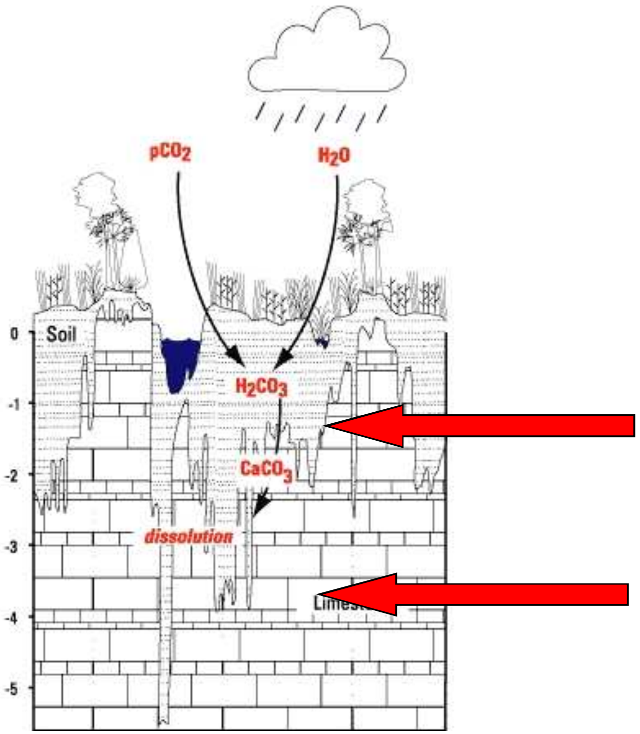
http://en.wikipedia.org/wiki/

Global distribution of limestone



https://en.wikipedia.org/wiki/Karst

Mechanism of limestone dissolution in karst



atmosphere → **$pCO_2 \approx 10^{-3.444}$ atm**

underground → **$pCO_2 >> 10^{-3.444}$ atm**

$2\ H_2O + 2\ CO_2\ (g) \leftrightarrow 2\ H_2CO_3^*(aq) \leftrightarrow 3\ H^+ + HCO_3^- + CO_3^{2-}$

(CO_2 dissolution, pH increase)

$3\ CaCO_3(s) + 3\ H^+ \leftrightarrow 3\ Ca^{2+} + HCO_3^- + CO_3^{2-} + H_2CO_3^*$

($CaCO_3$ dissolution)

(atmosphere → **$pCO_2 \approx 10^{-3.444}$ atm**)

$H_2CO_3^*(aq) \leftrightarrow 2\ H_2O + 2\ CO_2\ (g)$

(CO_2 degasification)

$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3(s)$

($CaCO_3$ precipitation)

Innovative Technologies and Sustainable Use of Mediterranean Sea Fishery and Biological Resources
(FishMed-PhD 37 2022-03-01)

Crystallization in Environment and Environmental Protection

D. Kralj
Ruđer Bošković Institute, Zagreb, Croatia

3. Calcium Carbonate precipitation and biomineralization

Research on $CaCO_3$ biomineralisation - implication on material science

Biomineralization – study of processes that lead to the formation of hierarchically structured organic–inorganic materials, generated by living organisms

Interdisciplinary – chemistry, biology, **materials science**...

Importance – paleontology, geology, geochemistry, biomedicine, ..., **materials science (!!)**

$CaCO_3$ biomineralization - marine, freshwater and terrestrial organisms
  Calcite (e.g. foraminifera, coccolithophores)
  Aragonite (e.g. corals)
  Aragonite and Calcite (e.g. bivalve shells)
  Vaterite and amorphous $CaCO_3$ (precursor phases, fish otoliths)

Relevance for materials science - production of advanced materials by simple process, at mild temperatures, pressure and chemical environment …

Shell formation in mollusks

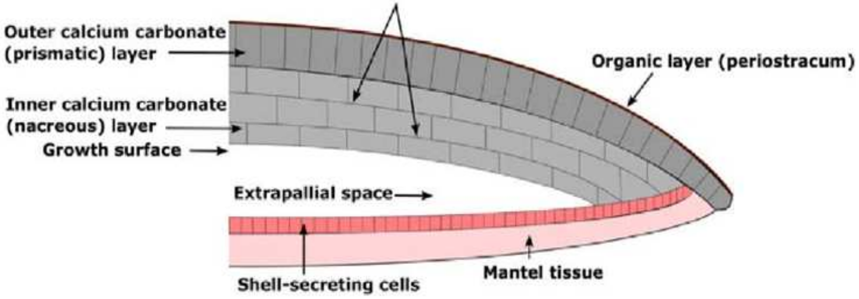
Molluscan shells → 95–99% calcium carbonate, 1–5 % organic component

Organic-inorganic composite → fracture toughness ≈ 3000 X greater than inorganic crystals (ADVANCED MATERIALS)

Soluble and insoluble (macro)molecules (proteins, sugars and lipids) → responsible for crystal nucleation and growth

Organic components → characteristic of specific mineral layer and of specific species

Different mineral layers → different polymorphs (calcite and aragonite)



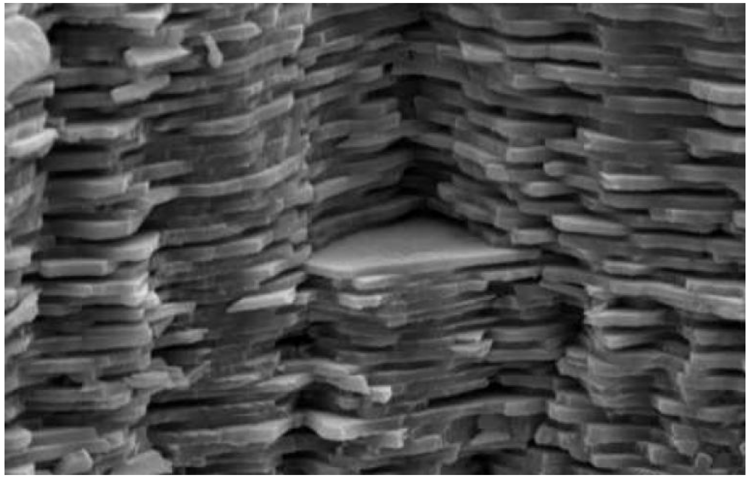
KELLY R. MARTIN et all. Teaching an Old Shell New Tricks: Extracting DNA from Current, Historical, and Ancient Mollusk Shells, BioScience 71: 235–248

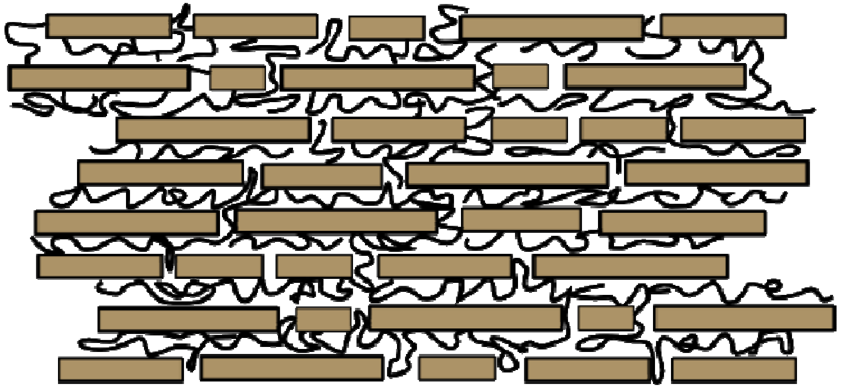
http://en.wikipedia.org/wiki/

Nacre

Inorganic component → aragonite platelets (10–20 µm wide, 0.5 µm thick) arranged in a continuous parallel lamina

Organic component → chitin, lustrin and silk-like proteins





http://en.wikipedia.org/wiki/

Research 1

Role of synthetic macromolecules in $CaCO_3$ biomineralization of mollusc shells

http://en.wikipedia.org/wiki/

Facts

Soluble macromolecules (**acidic glycoproteins** – reach in Asp and Glu) responsible for **polymorphism** in mollusk shells

Insoluble organic matrix – control the shape, size and aggregation of crystals

Amorphous $CaCO_3$– precursor phase to calcite or aragonite

Specific goals

Investigate interactions between mineral / organic additive by using **synthetic analogues** of natural macromolecules extracted from shells (poly-L-glutamic acid (pGlu), poly-L-aspartic acid (pAsp))

Investigate effects on

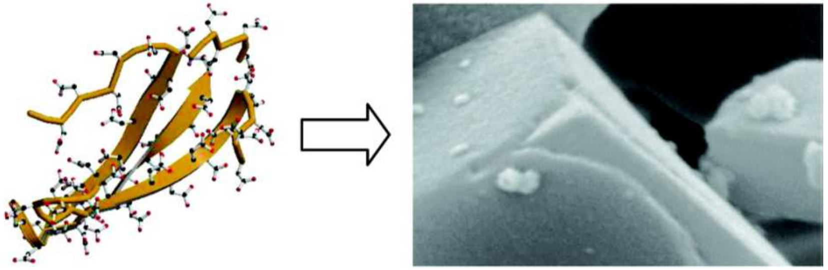
(1) crystal growth

(2) nucleation and

Apply "kinetic" approach to analysis of biomineralization, which is **complementary to structural** investigation

Hypothesis

Organic / inorganic interaction in biomineralization ≈ interfacial interactions crystal / macromolecules in precipitation systems



Precipitation model systems → **crystal growth**

(**1. Seed addition**)

Constituent ions

Lower supersaturation

$c_i(CaCl_2)_{aq.} = c_i(Na_2CO_3)_{aq.} = 1.0 \times 10^{-3}$ mol dm^{-3}

Higher supersaturation

$c_i(CaCl_2)_{aq.} = c_i(Na_2CO_3)_{aq.} = 2.5 \times 10^{-3}$ mol dm^{-3}

Additives

0.3 ppm < c_i(pAsp, pGlu) < 2.0 ppm

0.2 ppm < c_i (pLys) < 7.0 ppm

***Why simple** precipitation systems and simple model molecules (macromolecules)??*

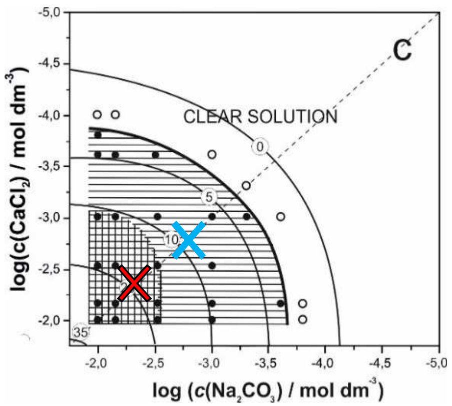
***Easy conclusion** about the basic molecular interactions at crystal/solution interfaces!!*

A. Precipitation diagram

constituent ions, no additives

$c_i(CaCl_2)_{aq.}$ = $c_i(Na_2CO_3)_{aq.}$ = 1.0×10^{-3} mol dm^{-3} → calcite (t_i > 5 min)

$c_i(CaCl_2)_{aq.}$ = $c_i(Na_2CO_3)_{aq.}$ = 2.5×10^{-3} mol dm^{-3} → vaterite (t_i > 5 min)



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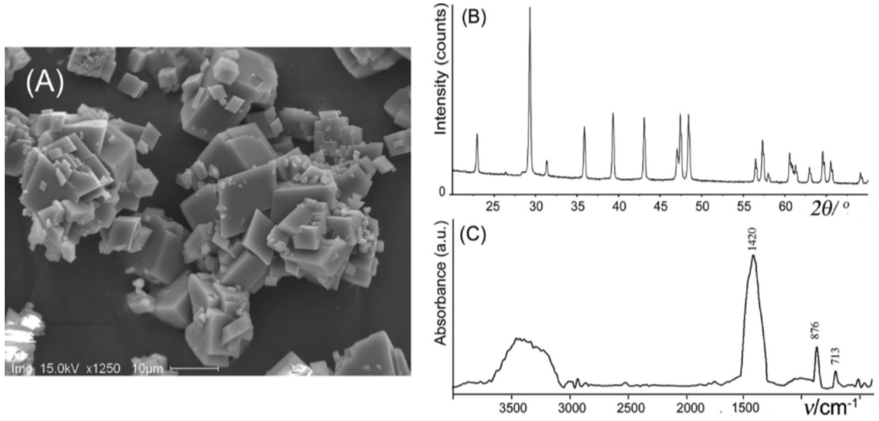
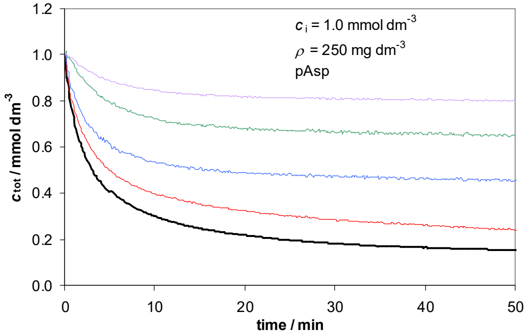


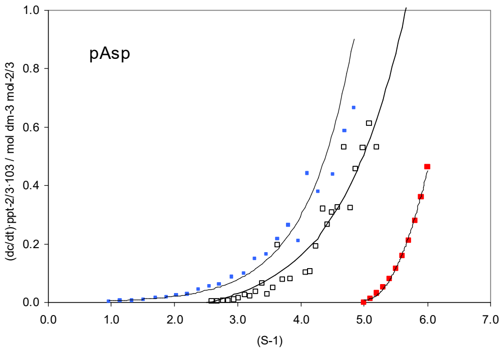
B. Crystal growth kinetics (growth mechanism)

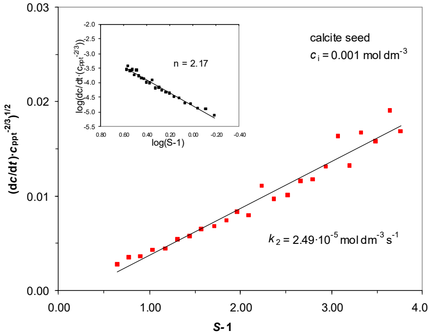
Kinetic curves (conc. vs. time)

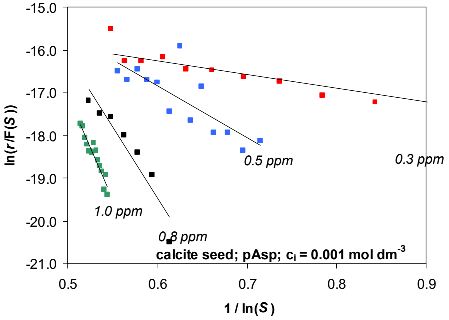
Growth rate (rate vs. S)

Testing theoretical mechanisms (**growth mechanism**)



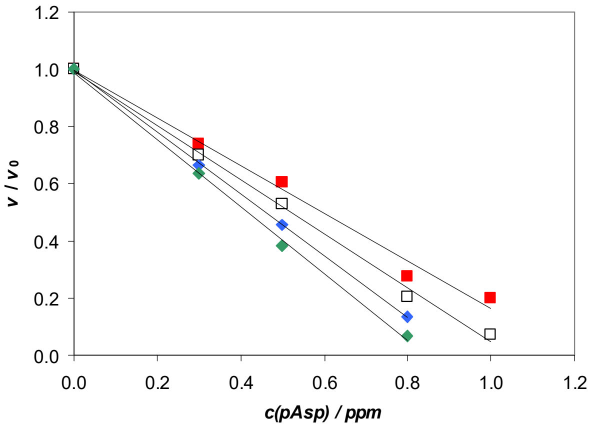






Testing inhibition potential of additives

$$\frac{v_{aditive}}{v_{model}}$$



Characterization of crystals and solution

Morphology (SEM)

pAsp

pGlu

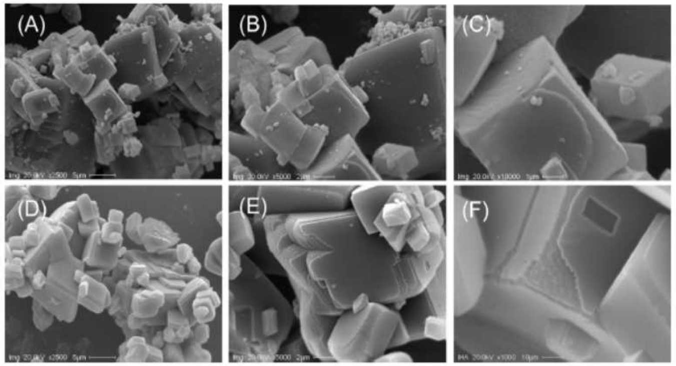


Figure 8. Scanning electron micrographs of calcite crystals after overgrowth experiments in the presence of pAsp (A−C) and pGlu (D−F).

model

pLys

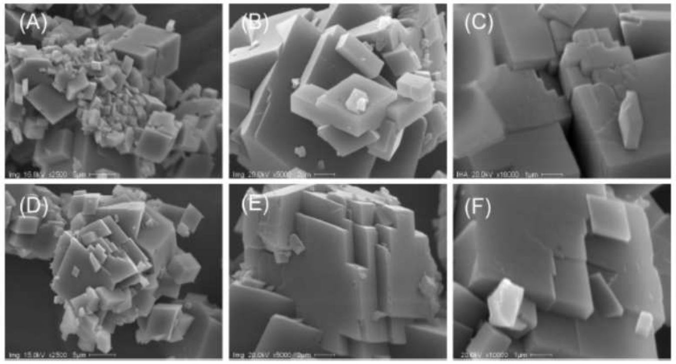
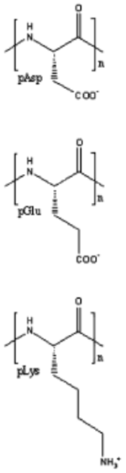
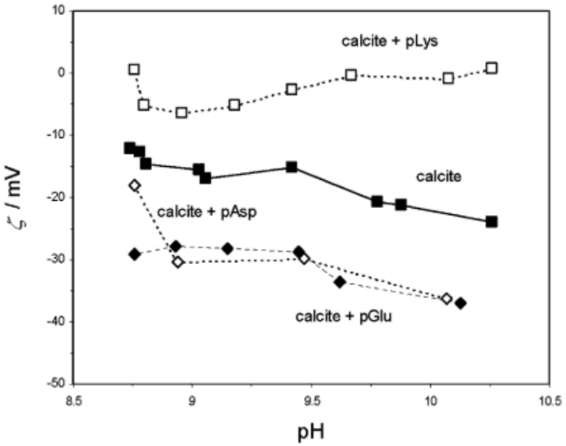


Figure 9. Scanning electron micrographs of calcite crystals after overgrowth experiments in the absence of additive (A−C) and in the presence of pLys (D−F).

Electrophoretic mobility (particle charge)





Precipitation model systems → **nucleation**

(**2. Spontaneous precipitation**)

Constituent ions

$c_i(CaCl_2)_{aq.} = c_i(Na_2CO_3)_{aq.} = 1.0 \times 10^{-3}$ mol dm^{-3}

$c_i(CaCl_2)_{aq.} = c_i(Na_2CO_3)_{aq.} = 2.5 \times 10^{-3}$ mol dm^{-3}

Additives

0.3 ppm < c_i(pAsp, pGlu) < 2.0 ppm

0.2 ppm < c_i (pLys) < 7.0 ppm

***Why simple** precipitation systems and simple model molecules (macromolecules)??*

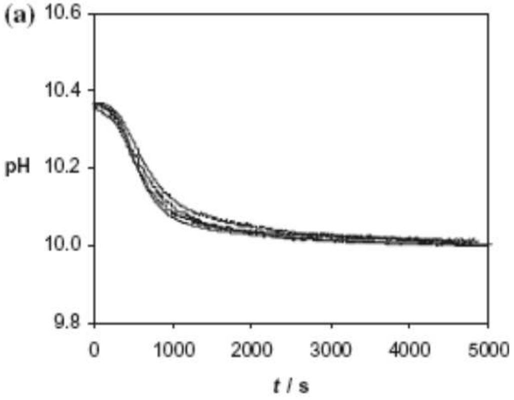
***Easy conclusion** about the basic molecular interactions at crystal/solution interfaces!!*

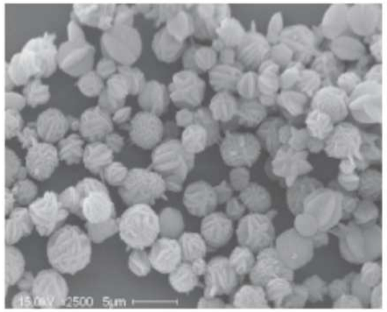
B. Crystal growth kinetics / spontaneous precipitation / **model system**

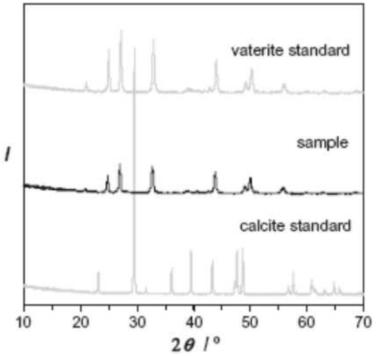
$c_i(CaCl_2)_{aq.} = c_i(Na_2CO_3)_{aq}$

1.0×10^{-3} mol dm^{-3}

Sc = 7.1





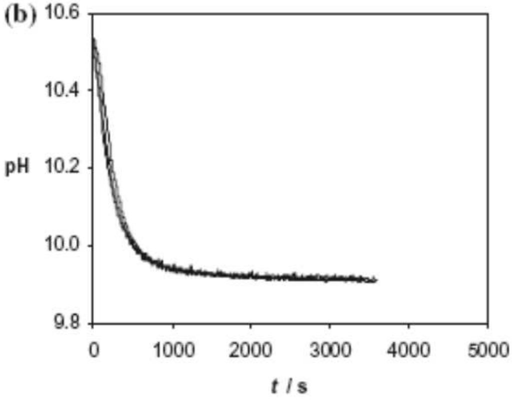


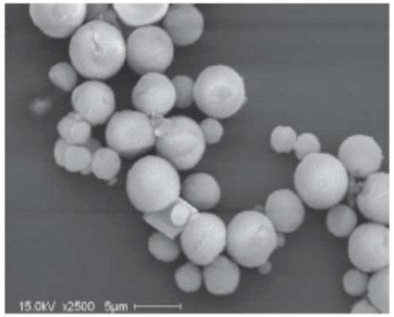
vaterite

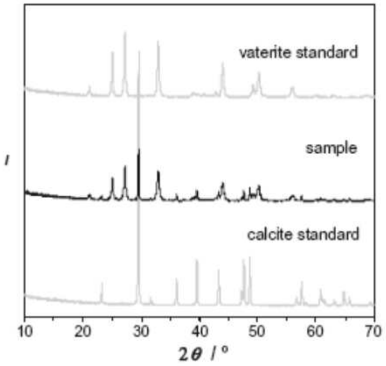
$c_i(CaCl_2)_{aq.} = c_i(Na_2CO_3)_{aq.}$

2.5×10^{-3} mol dm^{-3}

Sc = 13.7

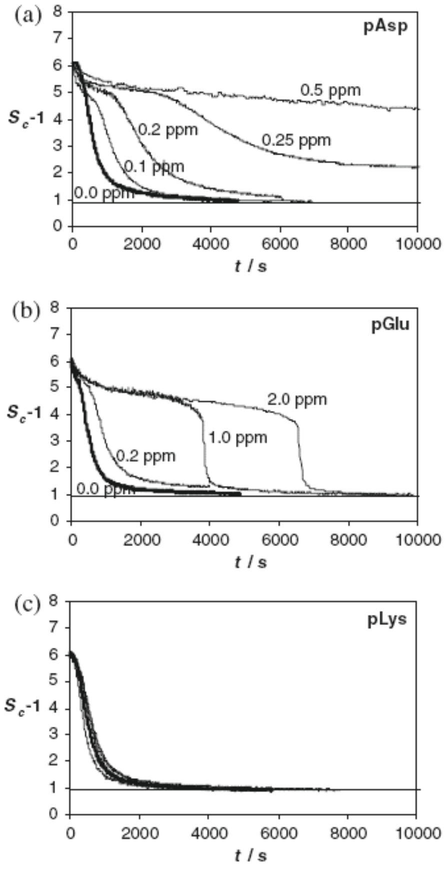






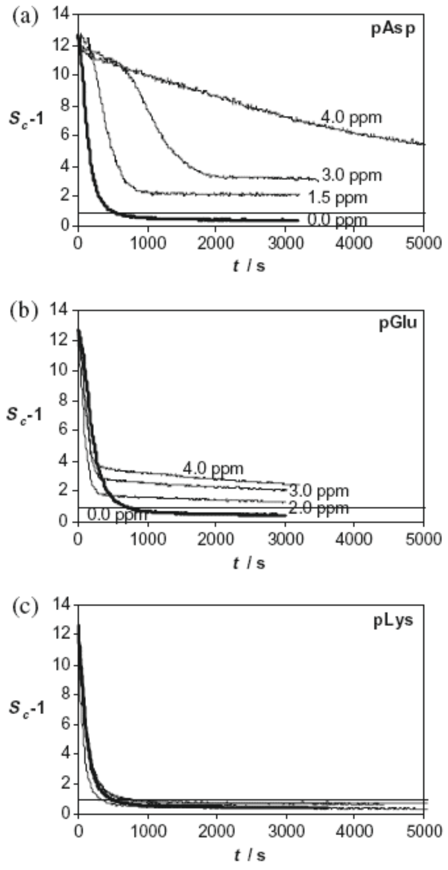
vaterite + calcite

B. Crystal growth kinetics / spontaneous precipitation / **additives**



$c_i(CaCl_2)_{aq.}$ = $c_i(Na_2CO_3)_{aq.}$ = 1.0×10^{-3} mol dm^{-3}

Sc = 7.1

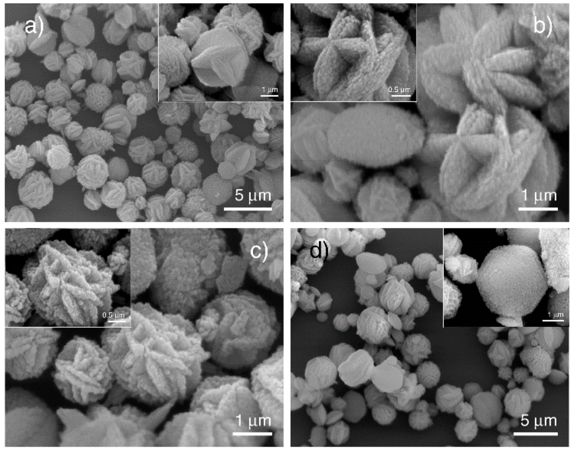


$c_i(CaCl_2)_{aq.}$ = $c_i(Na_2CO_3)_{aq.}$ = 2.5×10^{-3} mol dm^{-3}

Sc = 13.7

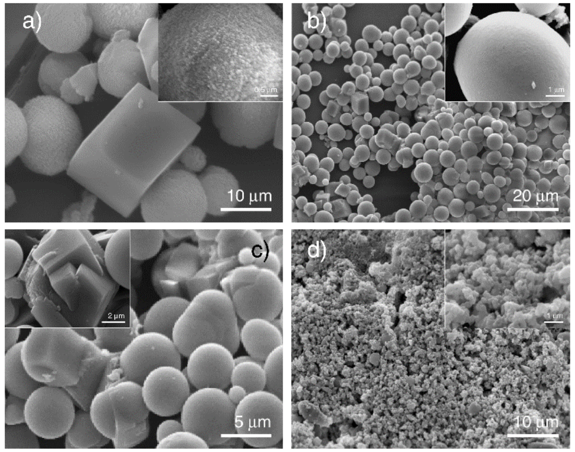
Characterization of crystals and solution

Morphology (SEM)



S_c = 7.1

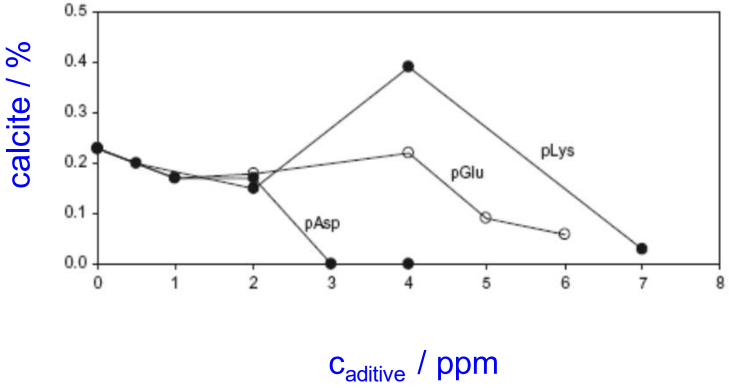
(a) 0 ppm pAsp
(b) 0.1 ppm pAsp
(c) 0.2 ppm pAsp
(d) 0.25 ppm pAsp



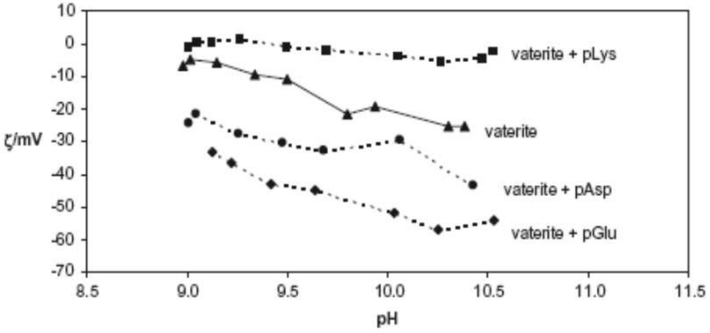
S_c = 13.7

(a) 0 ppm pAsp
(b) 1.0 ppm pAsp
(c) 1.0 ppm pAsp
(d) 4.0 ppm pAsp

Polymorphic composition



Electrophoretic mobility (particle charge) of vaterite



Conclusions

pGlu and pAsp – strong **inhibition of crystal growth** (coordinative binding to calcite surface??)

pAsp > pGlu

pAsp: partial β-pleated sheet; pGlu – random coil

pLys – dual action:

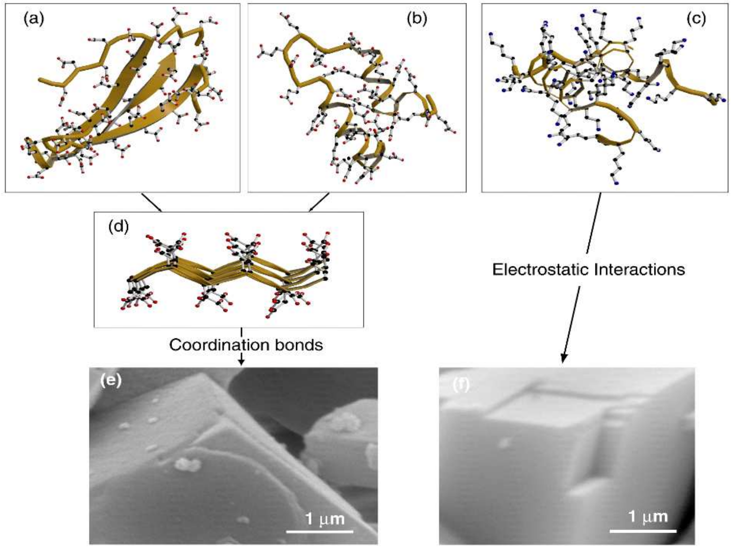
promotion at low concentration

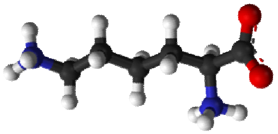
inhibition at high concentration (electrostatic binding to surface)

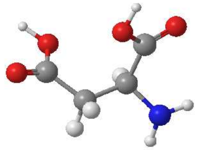
pAsp i pGlu – **inhbibition** of calcite **nucleation**

INH(pAsp) > INH(pGlu) >> INH(pLys)

Vaterite formation – kinetically controlled

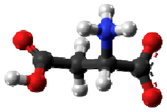


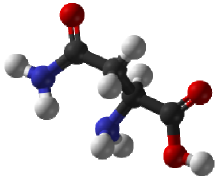


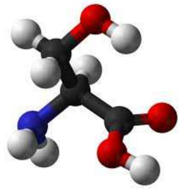


Research 2

Role of amino acids’ structure (charge, polarity) in $CaCO_3$ precipitation

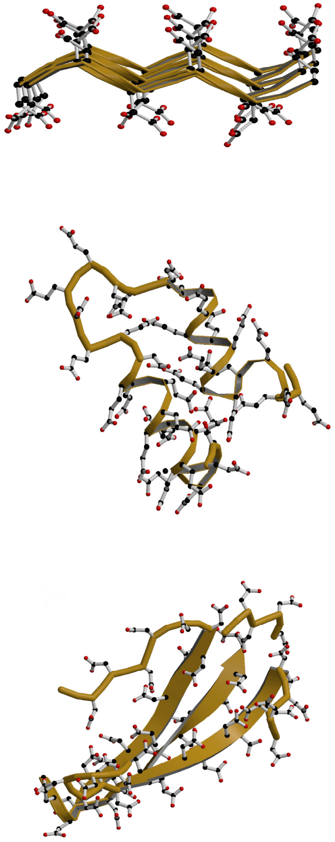


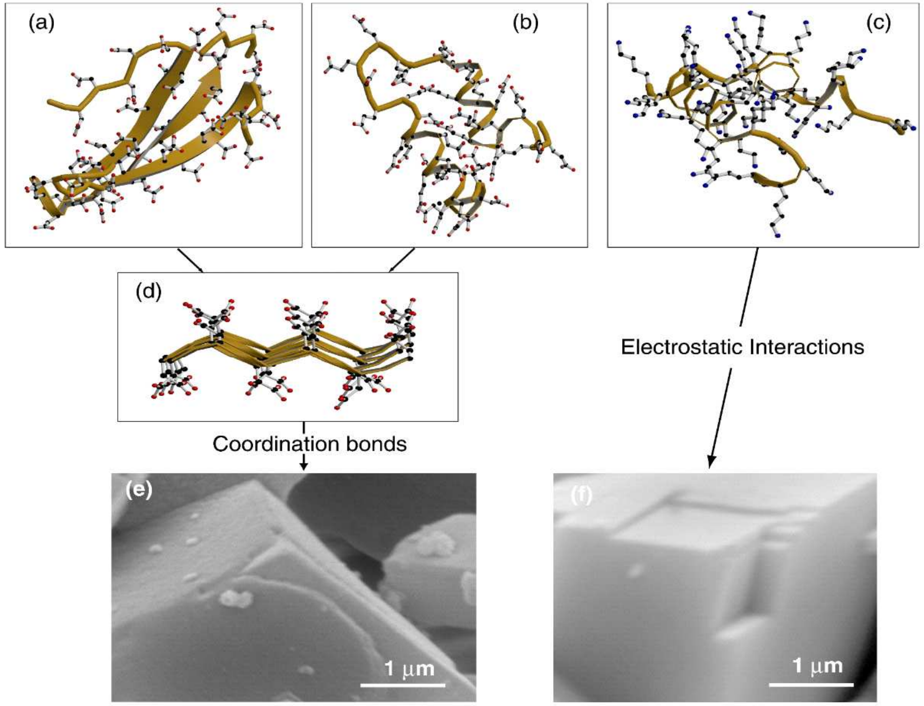


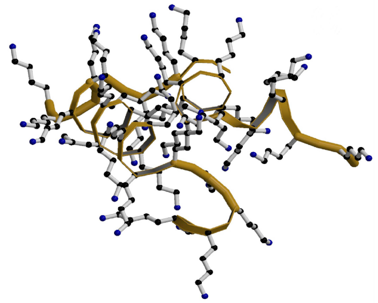


Motivation and hypothesis

Previously, not all possible interactions investigated
Deeper insight into basic molecular interactions of $CaCO_3$ and organic
Investigate role of hydrogen bonding donor side groups to additional interactions



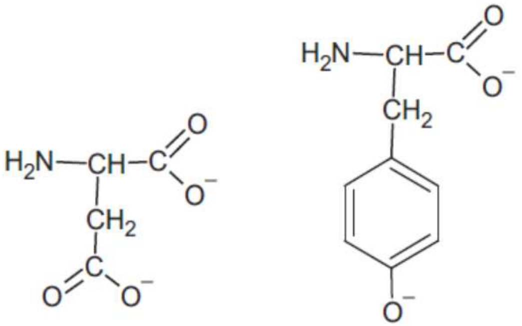




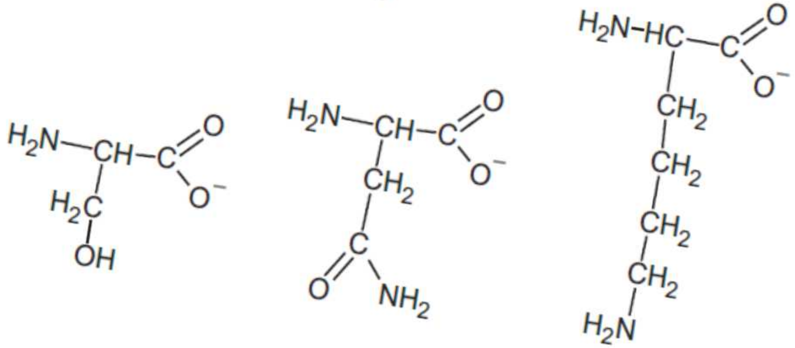
Selection of amino acids

Charge, polarity and chemical structure of side chains groups

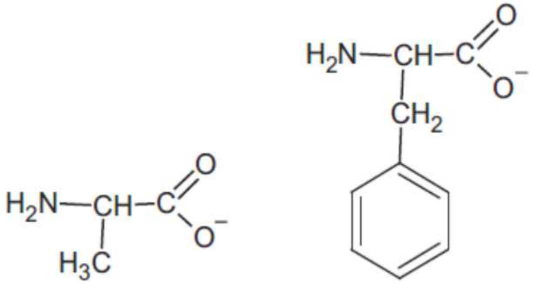
Asp, Tyr (pH = 10.7; negatively charged)



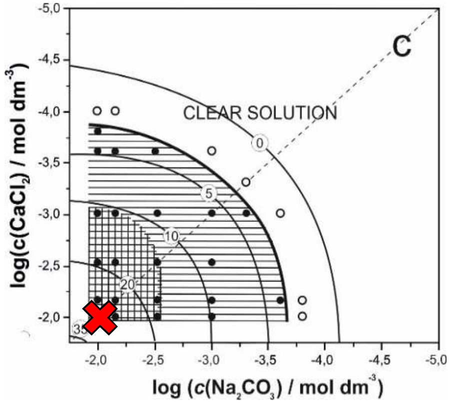
Ser, Asn, Lys, (pH = 10.7; polar, hydrogen bond donor)



Ala, Phe (pH = 10.7; non-polar and hydrophobic)



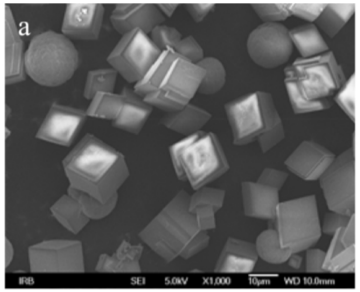
Spontaneous precipitation



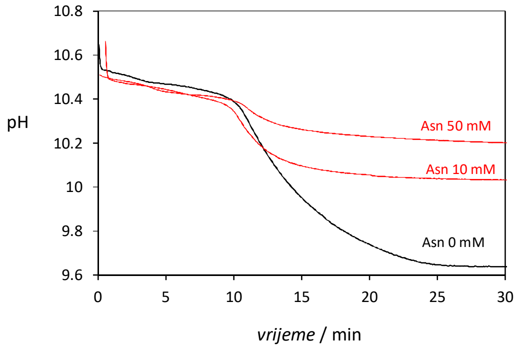
$c_i(Ca^{2+})$ = 0.01 mol dm^{-3}
$c_i(CO_3^{2-})$ = 0.01 mol dm^{-3}

10.0 mmol dm^{-3} < c_i(AA) < 75.0 mmol dm^{-3}
Asp, Tyr, Ala, Phe, Ser, Asn, Lys

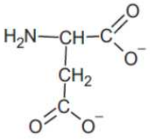
pH_i = 10.7
θ = 25 ° C, t = 30 min



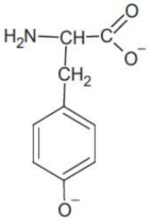
83% calcite + 17% vaterite



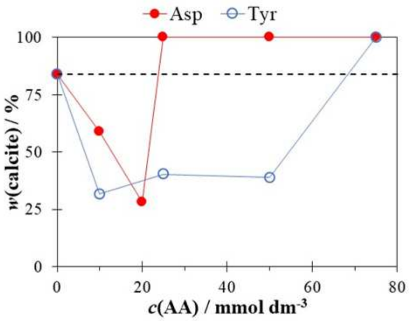
Polymorphic composition



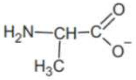
Asp



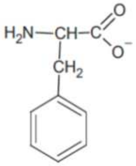
Tyr



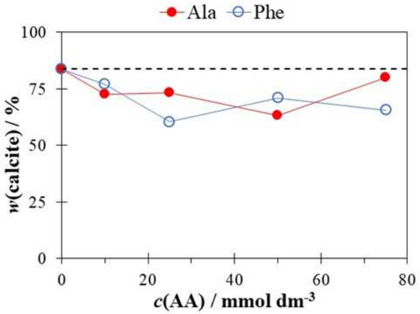
Negatively charged side chain



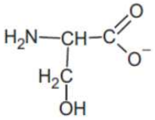
Ala



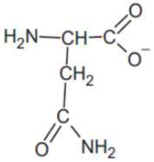
Phe



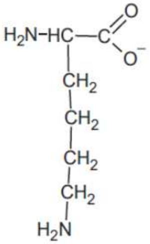
Hydrophobic side chain



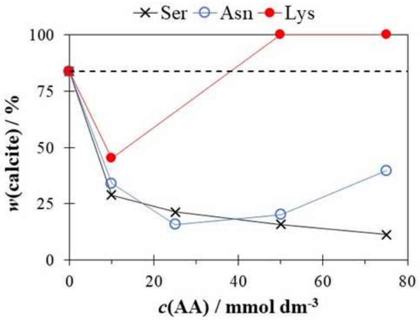
Ser



Asn

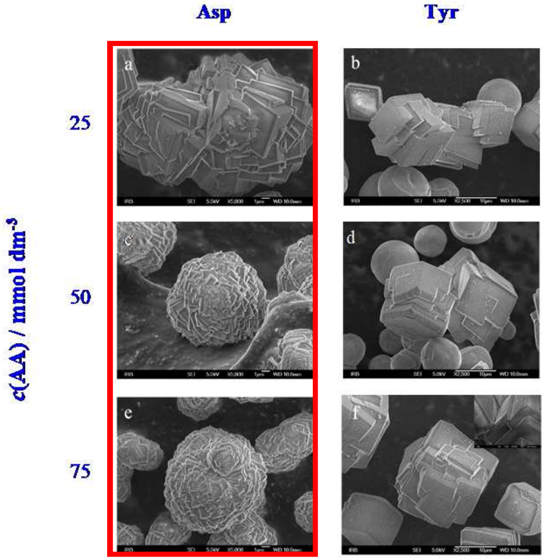


Lys

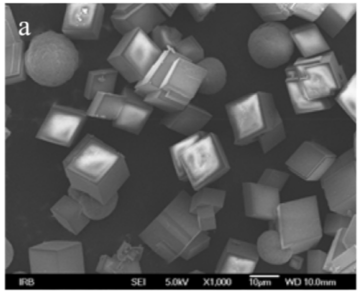


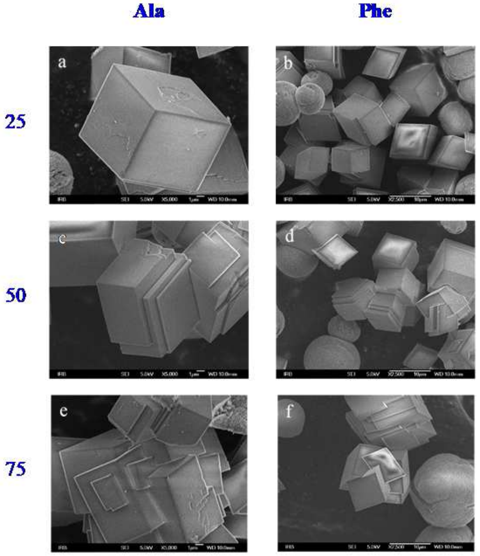
Polar side chain

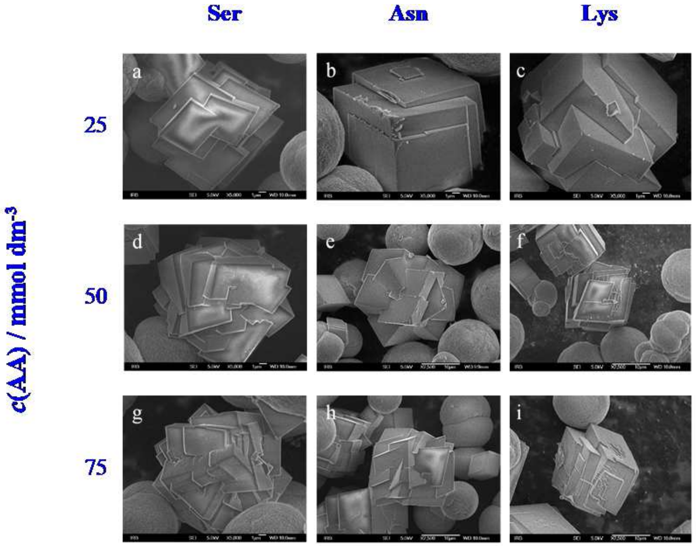
Morphology



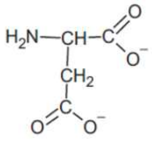
Referent

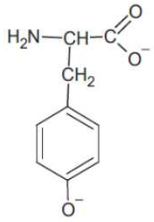


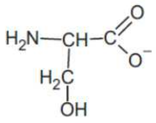


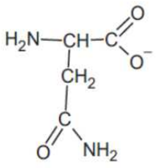


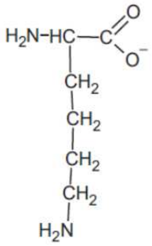
Calcite crystal lattice distortions

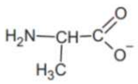

Asp

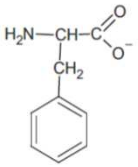

Tyr

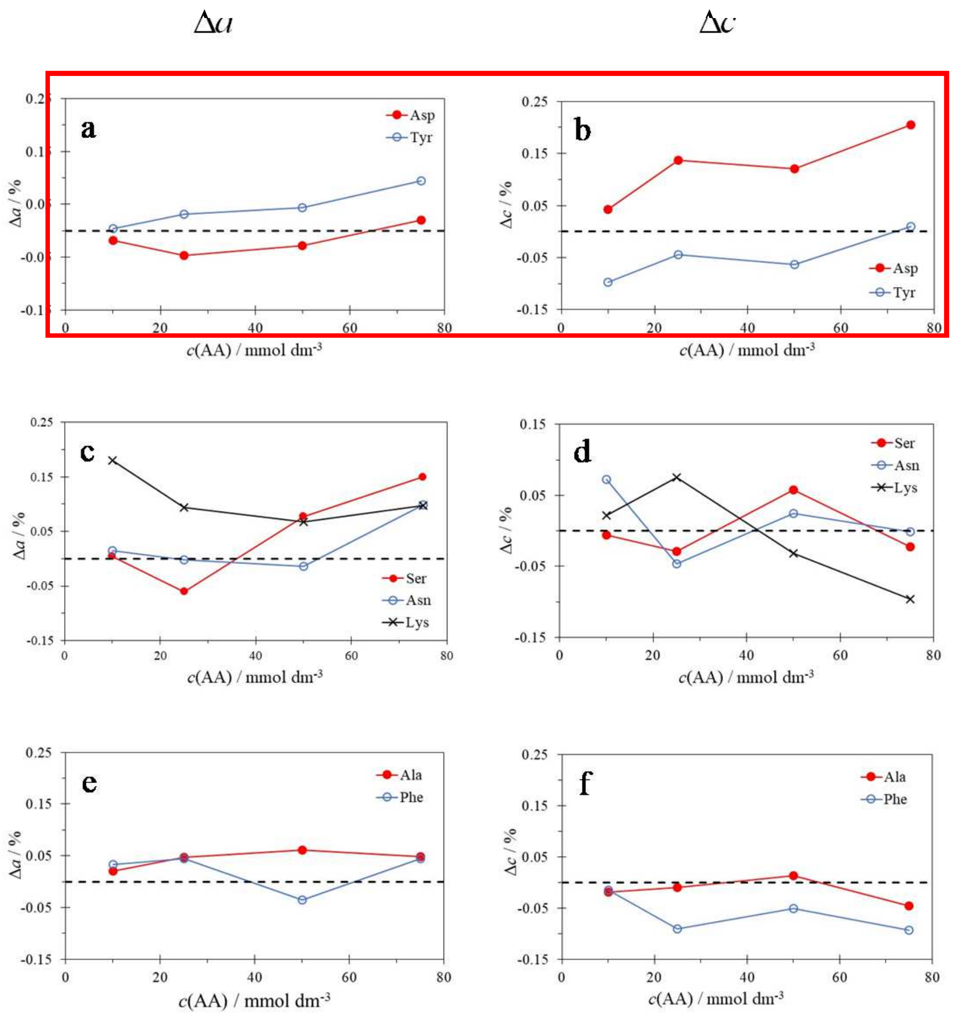

Ser


Asn

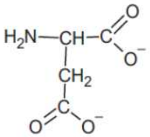

Lys


Ala

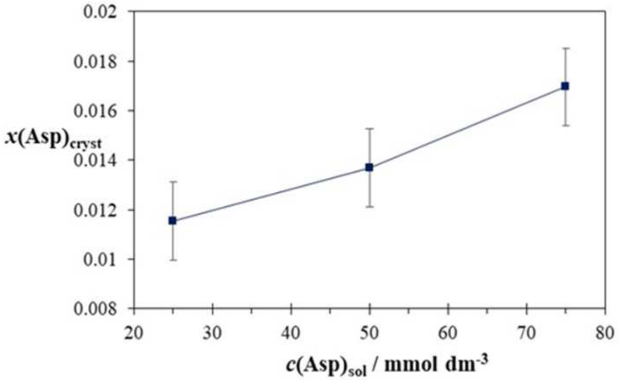

Phe

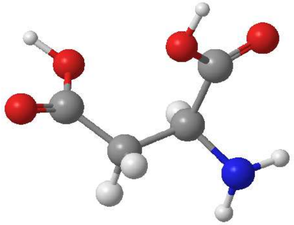


Asp incorporation into calcite lattice

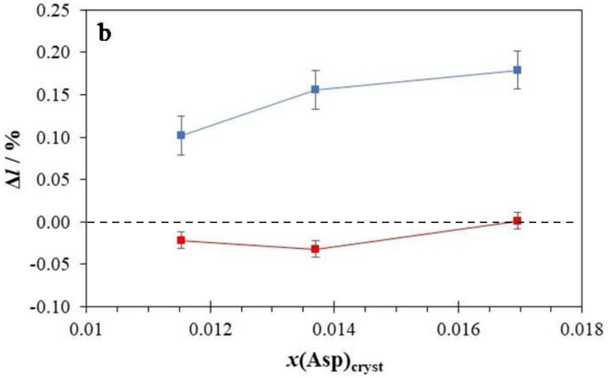


Asp





Relative changes of calcite crystal lattice



Δc

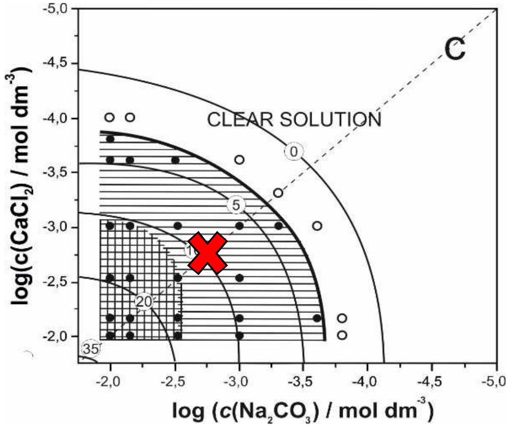
Δa

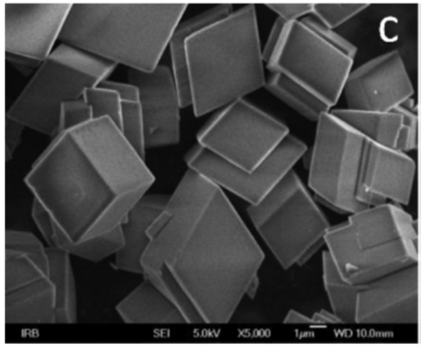
Seeded growth

$c_i(Ca^{2+}) = 0.001 \text{ mol dm}^{-3}$
$c_i(CO_3^{2-}) = 0.001 \text{ mol dm}^{-3}$

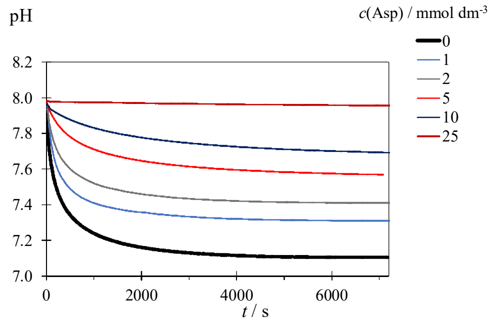
$10.0 \text{ mmol dm}^{-3} < c_i(AA) < 75.0 \text{ mmol dm}^{-3}$
Asp, Tyr, Ala, Phe, Ser, Asn, Lys

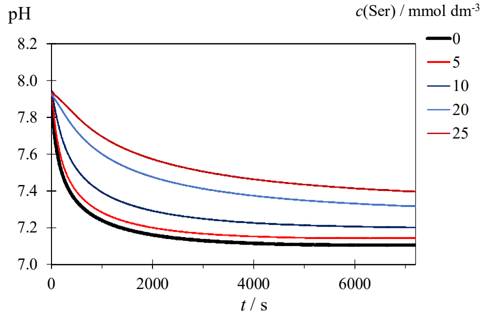
$\theta = 25 \text{ °C}$

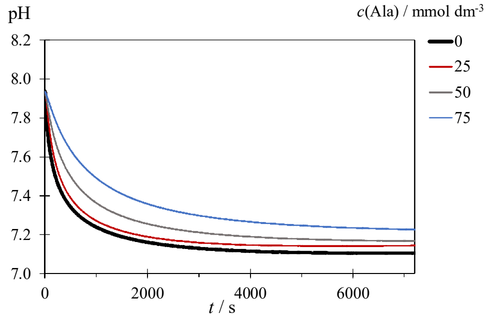




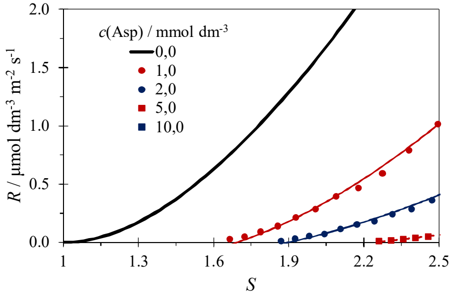
Progress curves

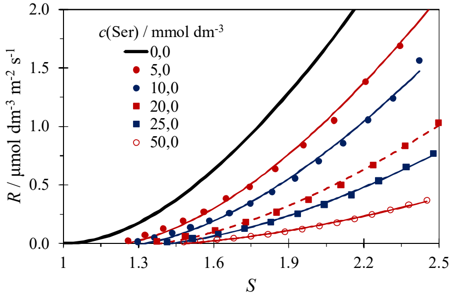


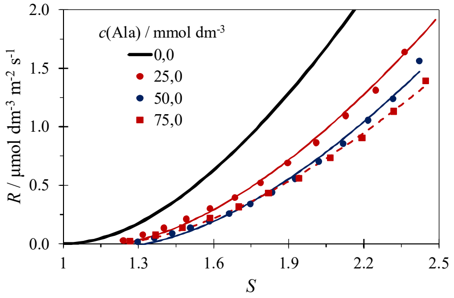




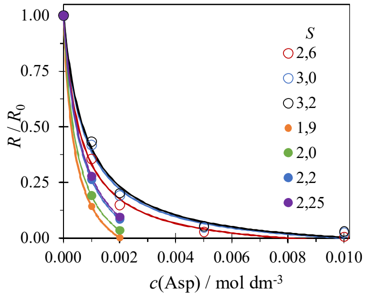
Growth rate vs S





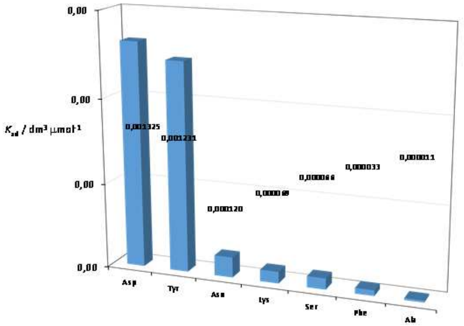


R/R_0 vs. c_{ad} analyses of additive interactions



Adsorption of amino acids, K_{ad}

Amino acid	**K_{ad} / dm^3 mmol^{-1}**
Asp	**0,001325**
Tyr	0,001231
Asn	0,000120
Lys	0,000069
Ser	0,000066
Phe	0,000033
Ala	0,000011



Asp, Tyr >> Ser, Asn, Lys > Ala, Phe

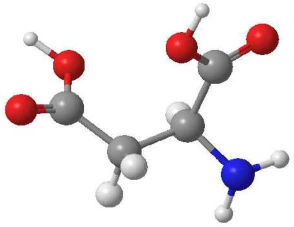
Conclusions

Non-polar amino acids (Phe, Ala) - insignificant effect on $CaCO_3$ precipitation

Charged and polar (hydrogen bonding) amino acids - (Asp, Tyr, Lys, Asn, Ser) changed the morphology, phase composition and crystal structure of the precipitates.

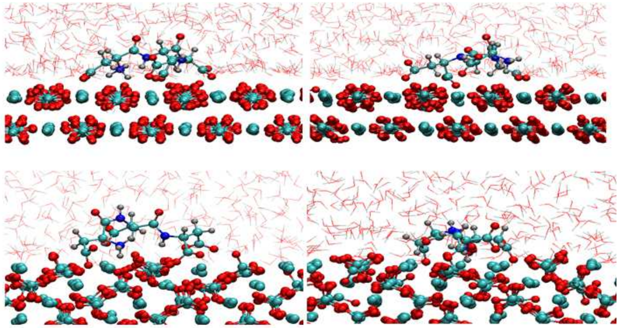
Asp had the **strongest effect** - significant change of calcite morphology and strong distortions of the crystal lattice.

Anisotropic distorsion of calcite ($\Delta c >> \Delta a$) - carboxylic groups on L-Asp substitute CO_3^{2-} and coordinate with Ca^{2+} ions from different layers in the crystal lattice.



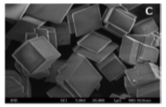
Relatively strong effect of polar AA may indicate that the **hydrogen bonding could influence** AA interactions with calcite surfaces during their diffusion on surface or along the step.

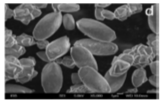
Next step in research ....

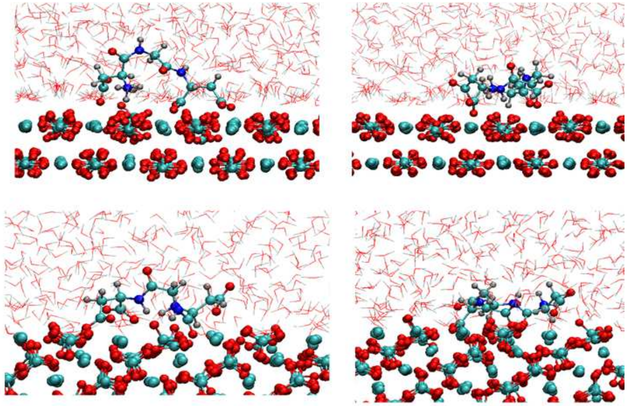


L-Asp-D-Asp-L-Asp

L-Asp-L-Asp-L-Asp

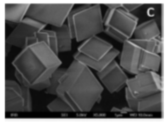


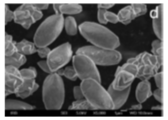




L-Asp-Gly-L-Asp

L-Asp-β-Ala-L-Asp





Research 3

Role of macromolecules in $CaCO_3$ biomineralization of corals

http://en.wikipedia.org/wiki/

Facts about corals

Biomineralization of aragonite - hard skeleton
Marine invertebrates - class Anthozoa of the phylum Cnidaria
Form compact colonies of many identical individual polyps
Reef builders

Colony of corals - genetically identical polyps
Individual colonies - grow by **asexual** reproduction of polyps
Breed sexually - by spawning

Energy and nutrients - from photosynthetic unicellular dinoflagellates (Zooxanthellae, genus Symbiodinium)
Zooxanthellae - live within coral tissues and give color - require sunlight

http://en.wikipedia.org/wiki/

Aragonite precipitation in c**orals** at **high** and **low supersaturation** conditions (higher growth rate during day-time, slower during night-time periods)
Spontaneous precipitation – nucleation of aragonite
Crystal growth – on preformed aragonite crystals
Complex precipitation system / medium (extrapallial solution)

Specific goals

Obtain (extract) soluble organic macromolecules (SOM) from
- Balanophyllia europaea (light sensitive)
- Leptopsammia pruvoti (light insensitive)

Apply "kinetic" approach to analyze biomineralization of aragonite

Discern a role of
- **Physicochemical parameters** (supersaturation)
- **Biological parameters** (role of SOM)
  - Spontaneous precipitation – nucleation (high supersaturation = day-time growth period, $S_a \approx 25$)
  - Seeded precipitation (aragonite) - crystal growth (low supersaturation = night-time growth period, $S_a \approx 3.2$)

Hypothesis

Different growth mechanisms during the night and day precipitation of aragonite in corals

Model species

Balanophyllia europea (Scarlet coral)

Small stony, solitary coral
Only in the Mediterranean Sea
Photophilous species (needs sunlight to maintain alive symbiotic micro-algae)

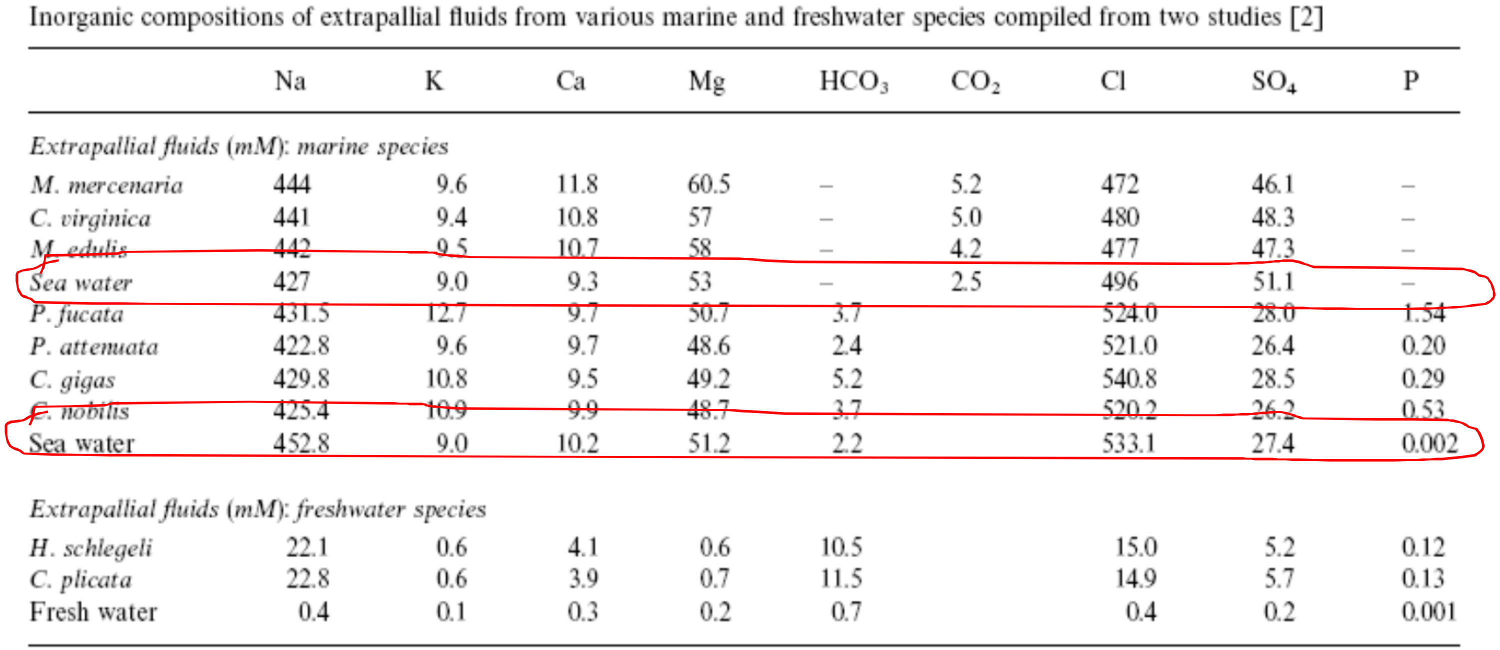
Leptopsammia pruvoti (Sunset cup coral)

Solitary stony coral
Azooxanthellate species (not contain the symbiotic unicellular algae)
Western Mediterranean Sea, Adriatic Sea,...

http://en.wikipedia.org/wiki/

Selection of model system?

Artificial seawater ≈ extrapallial fluid



Inorganic compositions of extrapallial fluids from various marine and freshwater species compiled from two studies [2]

	Na	K	Ca	Mg	HCO_3	CO_2	Cl	SO_4	P
Extrapallial fluids (mM): marine species									
M. mercenaria	444	9.6	11.8	60.5	–	5.2	472	46.1	–
C. virginica	441	9.4	10.8	57	–	5.0	480	48.3	–
M. edulis	442	9.5	10.7	58	–	4.2	477	47.3	–
Sea water	427	9.0	9.3	53	–	2.5	496	51.1	–
P. fucata	431.5	12.7	9.7	50.7	3.7		524.0	28.0	1.54
P. attenuata	422.8	9.6	9.7	48.6	2.4		521.0	26.4	0.20
C. gigas	429.8	10.8	9.5	49.2	5.2		540.8	28.5	0.29
C. nobilis	425.4	10.9	9.9	48.7	3.7		520.2	26.2	0.53
Sea water	452.8	9.0	10.2	51.2	2.2		533.1	27.4	0.002
Extrapallial fluids (mM): freshwater species									
H. schlegeli	22.1	0.6	4.1	0.6	10.5		15.0	5.2	0.12
C. plicata	22.8	0.6	3.9	0.7	11.5		14.9	5.7	0.13
Fresh water	0.4	0.1	0.3	0.2	0.7		0.4	0.2	0.001

S. L. Tracy et al., Journal of Crystal Growth 193(1998)374-381

Model systems

Spontaneous precipitation (ASW-1)

$c((\mathrm{Na_2CO_3})/(\mathrm{NaHCO_3})) = 5\cdot10^{3}$ mol dm^{3}
$c(\mathrm{CaCl_2}) = 0.01$ mol dm^{3}
$c(\mathrm{MgCl_2}) = 0.05$ mol dm^{3}
$c(\mathrm{NaCl}) = 0.3$ mol dm^{3}
$\mathrm{pH_i} \approx 10.2$; $S_a \approx 11$

Seeding precipitation (ASW-2)

$c((\mathrm{Na_2CO_3})/(\mathrm{NaHCO_3})) = 5\cdot10^{3}$ mol dm^{3}
$c(\mathrm{CaCl_2})=0.01$ mol dm^{3}
$c(\mathrm{MgCl_2})=0.05$ mol dm^{3}
$c(\mathrm{NaCl})= 0.3$ mol dm^{3}
$\mathrm{pH_i} \approx 8.9$; $S_a \approx 5.8$

0.5 ppm $< c_i$(SOM-Beu) < 8 ppm
1 ppm $< c_i$(SOM-Lpr) < 8 ppm

$\theta = 21$ ° C, $t = 30$ min

Ionic equilibrium of relevant ionic species:

$\mathrm{H^+}$, $\mathrm{OH^-}$, $\mathrm{Ca^{2+}}$, $\mathrm{CaCO_3^0}$, $\mathrm{CaHCO_3^+}$, $\mathrm{H_2CO_3^*}$, $\mathrm{HCO_3^-}$, $\mathrm{CO_3^{2-}}$,
$\mathrm{Mg^{2+}}$, $\mathrm{MgCO_3^0}$, $\mathrm{MgHCO_3^+}$, $\mathrm{Cl^-}$, $\mathrm{Na^+}$

Initial conditions:

$[\mathrm{Ca}]_{tot}$, $[\mathrm{Mg}]_{tot}$, $[\mathrm{Na}]_{tot}$, $[\mathrm{Cl}]_{tot}$

Measurements:

pH

Spontaneous precipitation – nucleation of aragonite (ASW-1)

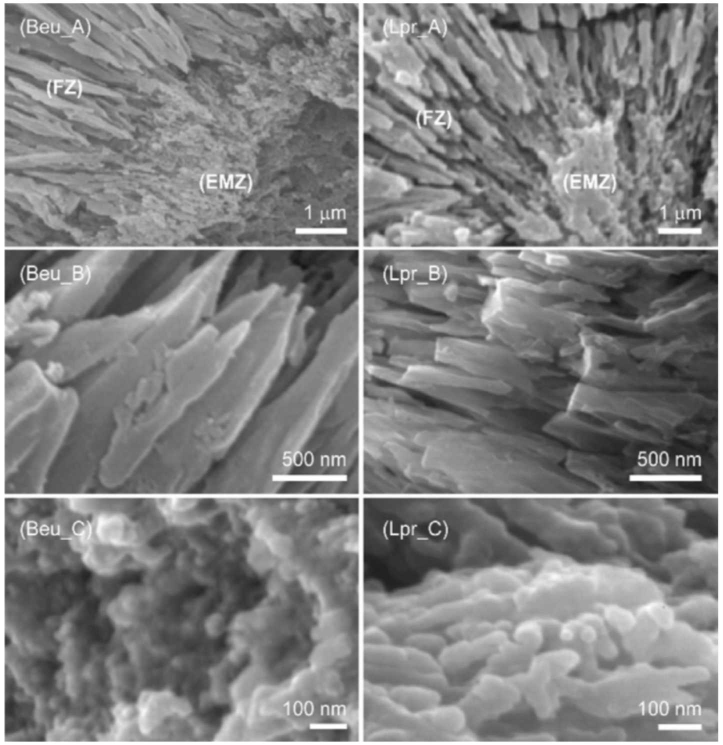
Morphology, size and polymorphism

SEM - cross sections of septum skeletons (aragonite)

B. europaea
L. pruvoti

Fiber zone (FZ)

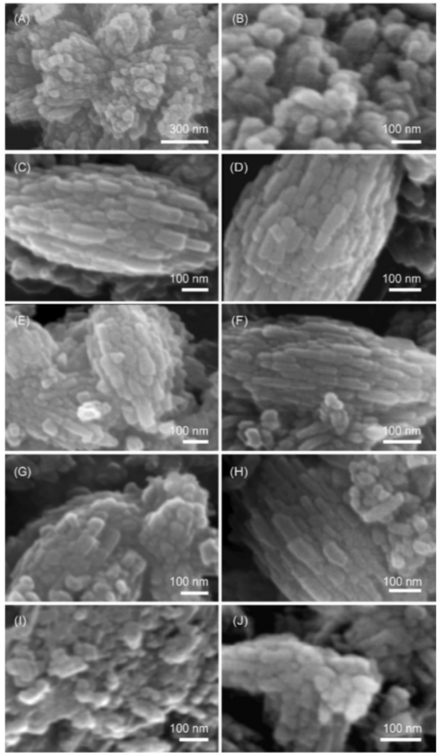
Early mineralization zone (EMZ)



SEM – *in vitro* spontaneous aragonite precipitation

SOM-Beu
SOM-Lpr

0.0 ppm
0.5 ppm
1.0 ppm
2.0 ppm
5.0 ppm

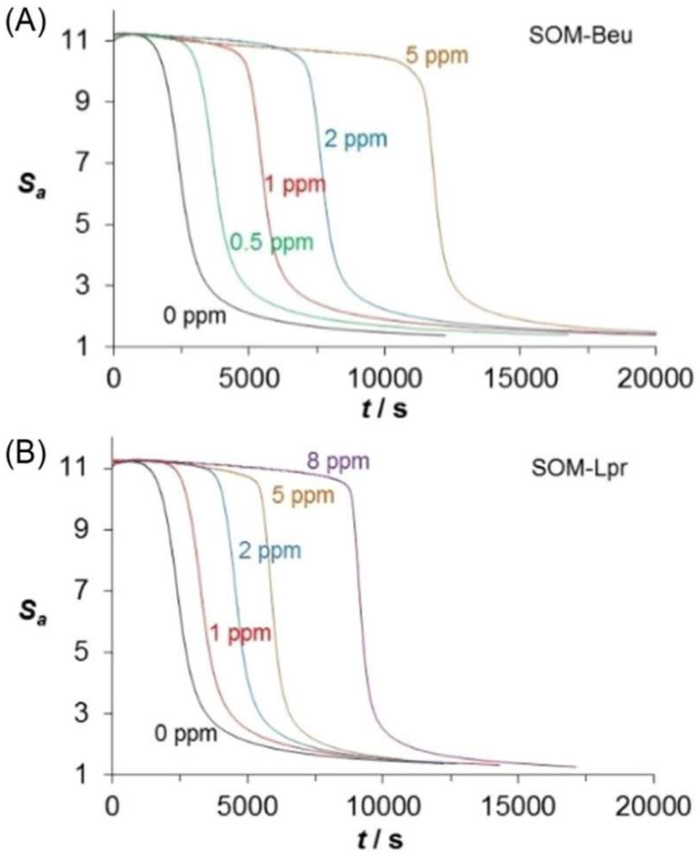


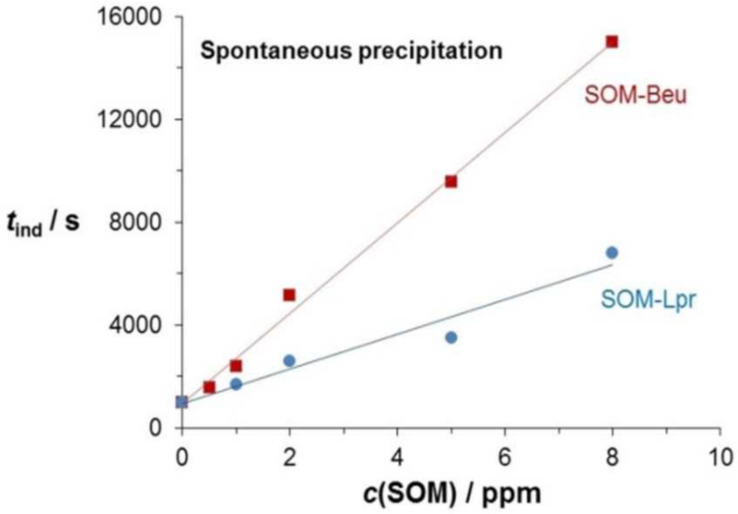
0.0 ppm
1.0 ppm
2.0 ppm
5.0 ppm
8.0 ppm

Highest concentrations of SOM → similarity with corals EMZ ?!

Spontaneous precipitation – nucleation of aragonite (ASW-1)

Induction time



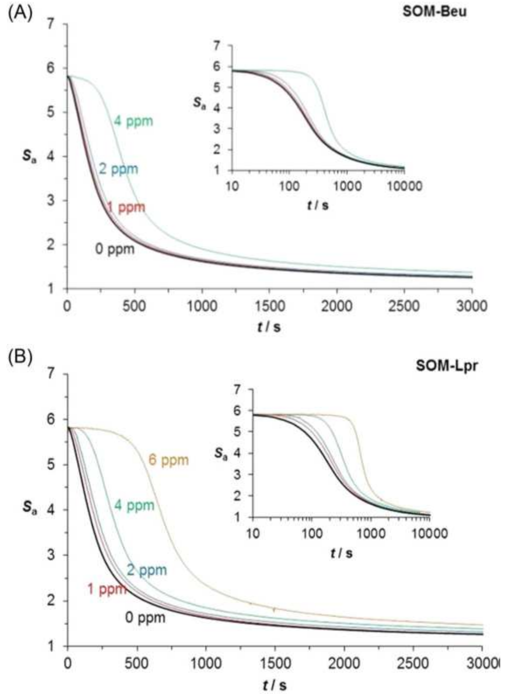


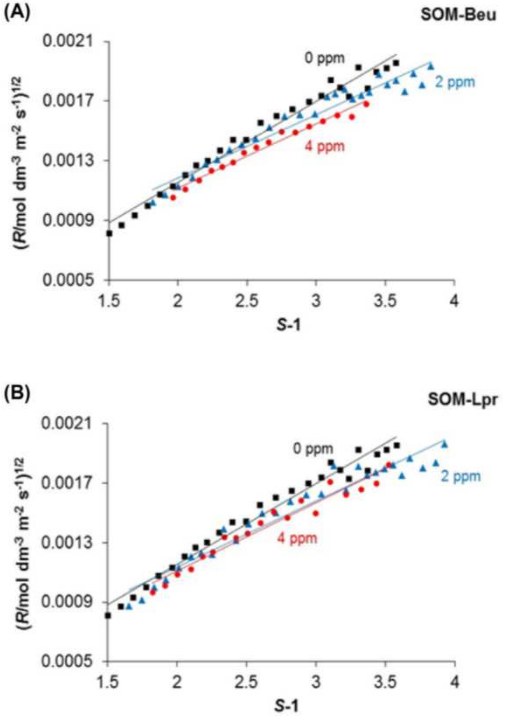
- Adsorption of SOM on nuclei and crystals!
- No change of mineralogical composition (aragonite)!
- Increased induction time with increasing concentration!

Seeded precipitation – crystal growth of aragonite (ASW-2)

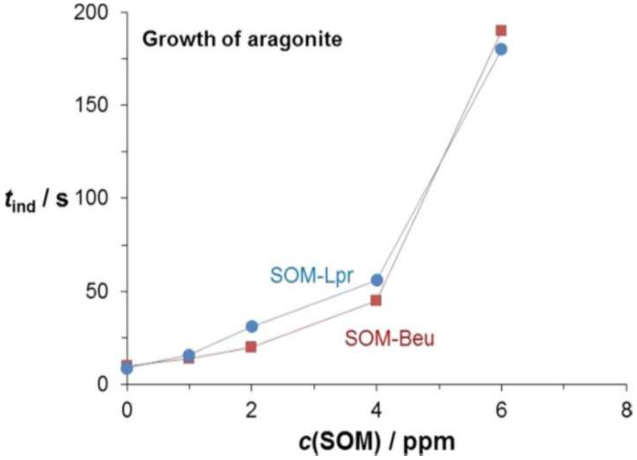
Kinetics

Growth kinetics → Growth mechanisms





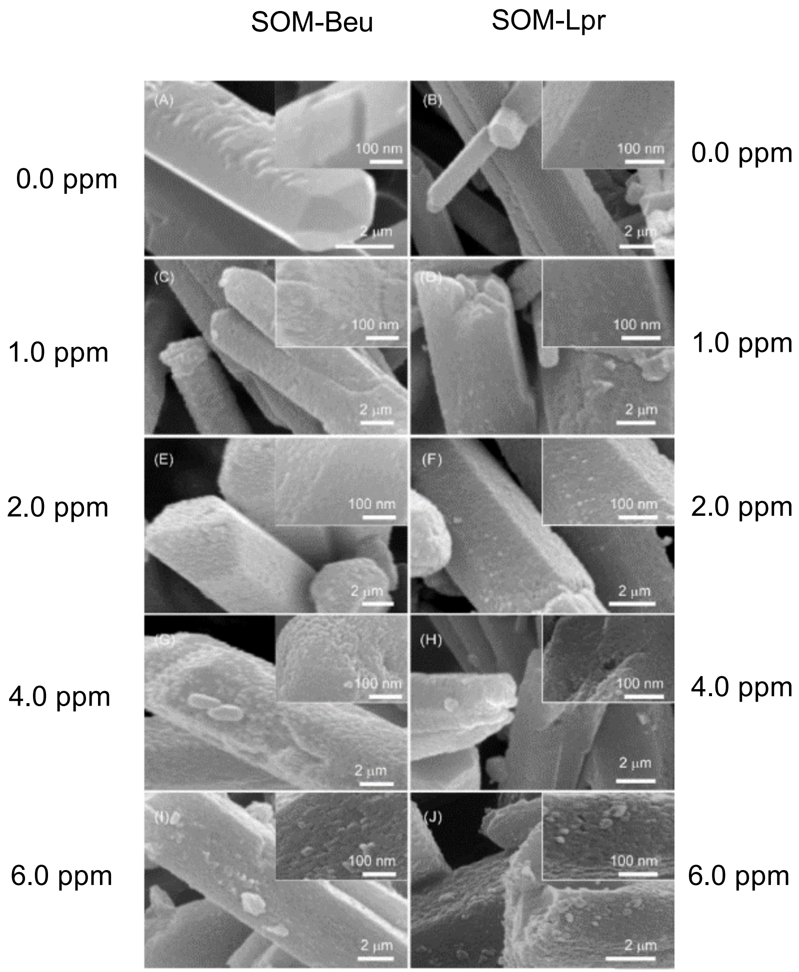
Induction time



- Adsorption of SOM on nuclei and crystals!
- No change of mineralogical composition (aragonite seed)!
- No change of growth mechanisms
- Inhibition increase with SOM concentration
- Increased induction time with increasing concentration!

Seeded precipitation – crystal growth of aragonite (ASW-2)

Morphology, size and polymorphism



- Seed – regular prismatic aragonite
- No change of mineralogical composition after overgrowth in presence of SOM
- No change of morphology at low SOM concentrations
- Increased roughness at higher SOM concentrations
- Highest Beu concentration - textural reorganization of particles

Conclusions

- Under **high supersaturation** conditions - **significant incorporation** of macromolecules into **mineral phase** during the nucleation and growth of crystals.

- **SOMs incorporate in aragonite**, but **not in calcite** crystals under similar conditions.

- Precipitated aragonite appears as aggregates of nanoparticles resembling those observed in the EMZs.

- Inhibition of precipitation observed as a systematic increase of induction period with increasing SOM addition

- The growth mechanism of aragonite obtained by seeding experiments (growth on the spiral step), did not change after the addition of SOM. However, the presence of high concentration of SOMs induces a change in the morphology and shape of the growing crystalline units.

- **Inhibition activity of SOM-Beu is stronger than that of SOM-Lpr**

- **Calcification of corals is controlled by both, pure physical-chemical mechanism (supersaturation) and biological mechanism** - two-step mode of growth, according to which the SOM plays an active role in the process.

Innovative Technologies and Sustainable Use of Mediterranean Sea Fishery and Biological Resources
(FishMed-PhD 37 2022-03-01)

Crystallization in Environment and Environmental Protection

D. Kralj
Ruđer Bošković Institute, Zagreb, Croatia

4. Crystallization in Environmental Protection

GLOBAL WARMING (GREENHOUSE EFFECT CAUSED BY CO_2 EMISSION IN ATMOSPHERE)

- **Anthropogenic CO_2 emission** - 40 Gt / year
- **78 %** of total anthropogenic – **industry**
- Currently in atmosphere – **410 ppm** CO_2
- By 2050 – more than **800 ppm** – ”Point of no return”

http://en.wikipedia.org/wiki/

Carbon (CO_2) capture and storage (CCS)

- **CO_2 capture** - from large point sources (coal-fired power plants, chemical plants, biomass power plants, cement production, steelmaking...) before entering the atmosphere
- **CO_2 Liquefaction -** long-term **storage** in deep geological formation (possible leak into atmosphere)
- **Expensive** process (cheap product: CO_2)

Alternative!!

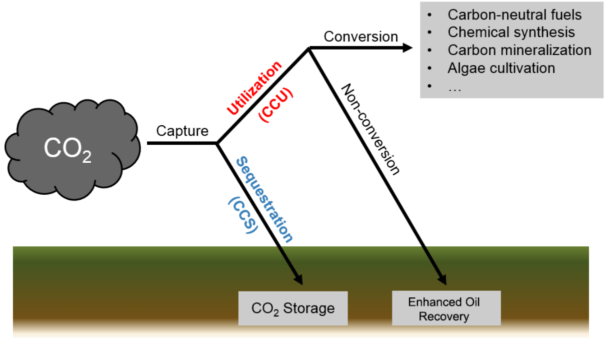
Carbon (CO_2) capture and utilization (CCU)

- **CO_2 capture** and **use** – production of high-value chemicals
- **Efficient technologies for CO_2** absorption into alkaline solution (monoethanolamine, NaOH, LiOH...)

  CO_2 + $RNH_2 \rightleftharpoons$ RNHCOOH (2) RNHCOOH + $RNH_2 \rightleftharpoons RNHCOO^- + RNH_3^+$

  CO_2 (g) + H_2O (aq) + 2 NaOH (aq) $\rightleftharpoons$ Na_2CO_3 (aq)+ 2 H_2O (aq)
- **Fixation by $CaCO_3$** precipitation

  (waste CO_2 + waste (blast furnace slag, containing CaO) → $CaCO_3$)



http://en.wikipedia.org/wiki/

Precipitated Calcium Carbonate

Versatile product with high added value in comparison to grounded $CaCO_3$

Application

- Filler in plastics
- Filler in paints
- Filler in food and pharma industry
- Fertilizer
- Glass, ceramic production
- Filler and coating in paper industry

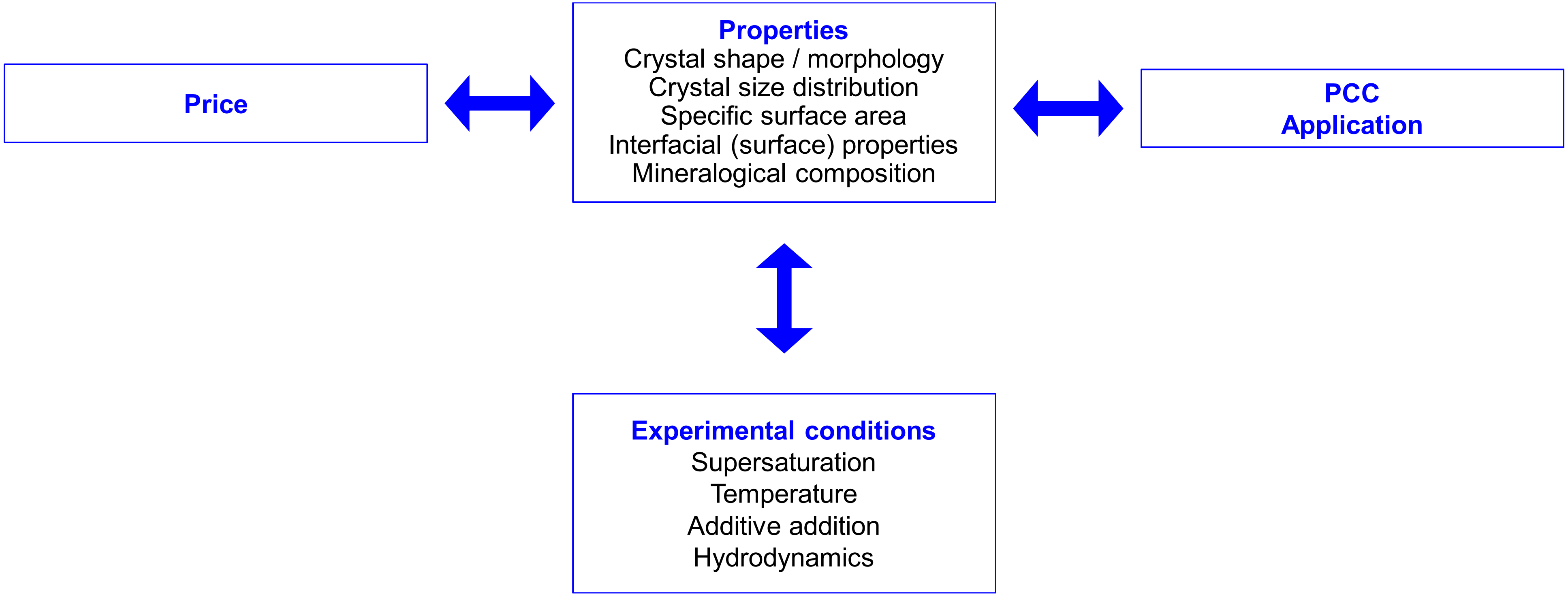
http://en.wikipedia.org/wiki/

Research 1

Rational control of critical calcite properties by selected experimental conditions

Precipitated calcium carbonate

Physical chemical properties vs. Technological parameters



Price

Properties
Crystal shape / morphology
Crystal size distribution
Specific surface area
Interfacial (surface) properties
Mineralogical composition

PCC
Application

Experimental conditions
Supersaturation
Temperature
Additive addition
Hydrodynamics

SELECTION OF MODEL SYSTEM

$$Ca^{2+}\ (l) + CO_3^{2-}\ (l) \rightleftarrows CaCO_3\ (s)$$

What about co-ions????? Cl^-, NO_3^-, SO_4^{2-}…. Na^+, K^+, NH_4^+, ….

PRECIPITATION MODEL SYSTEM
$Ca(OH)_2(l)$-$H_2CO_3(l)$-H_2O

$$Ca(OH)_2\ (l) + H_2CO_3\ (l) \rightleftarrows CaCO_3\ (s) + H_2O$$

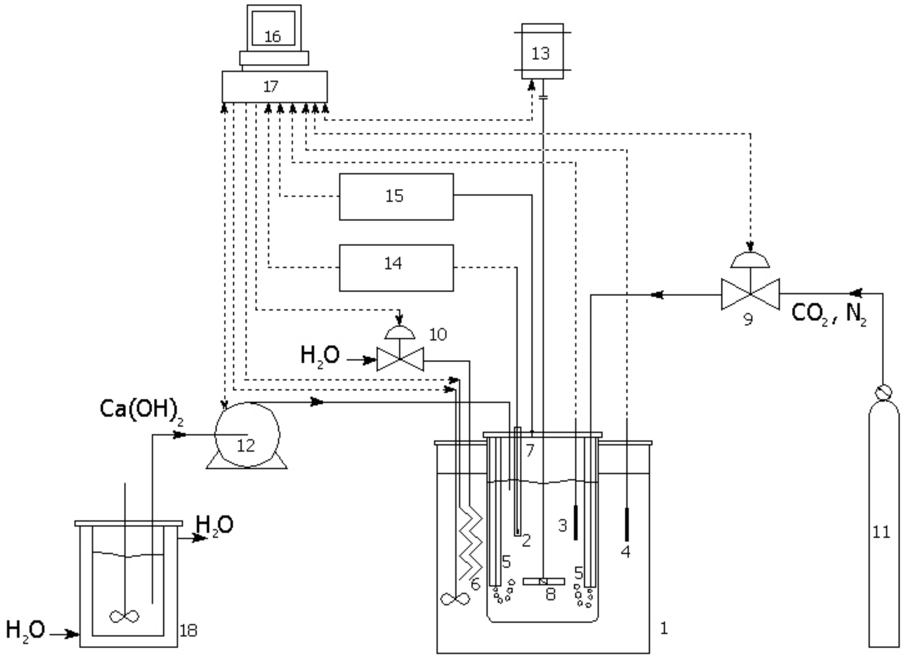
H^+, OH^-, Ca^{2+}, $CaCO_3^0$, $CaHCO_3^+$, HCO_3^-, CO_3^{2-}

(Only constituent ions and H_2O autoprotolysis!!)

$0.002\ \text{mol dm}^{-3} < c_i(Ca(OH)_2) < 0.010\ \text{mol dm}^{-3}$
$0.002\ \text{mol dm}^{-3} < c_i(H_2CO_3) < 0.010\ \text{mol dm}^{-3}$
$\theta = 25\ ^\circ C$

Impurities (Mg^{2+}, SO_4^{2-}, Cl^-, NO_3^-)

ANALYSES:
chemical / mineralogical
particle size distribution
morphology

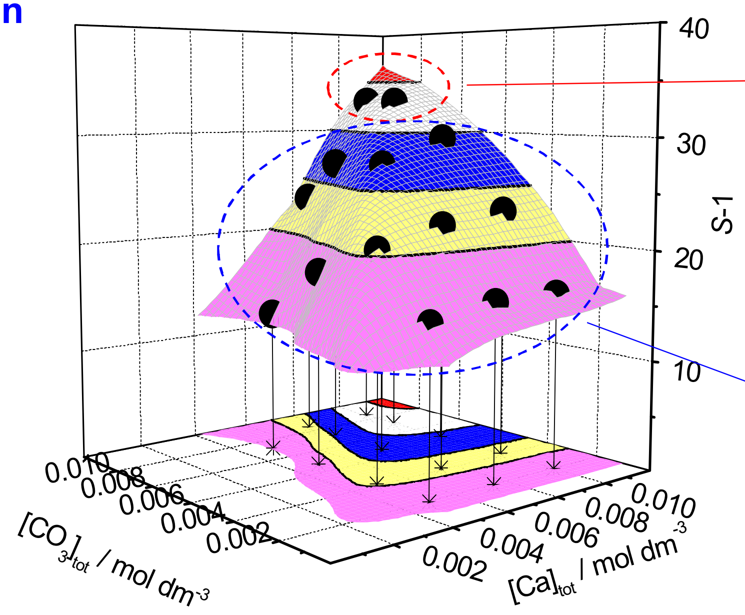


A. Precipitation diagram construction

Mixing $Ca(OH)_2$ (*l*) and H_2CO_3 (*l*)

aging for 20 min

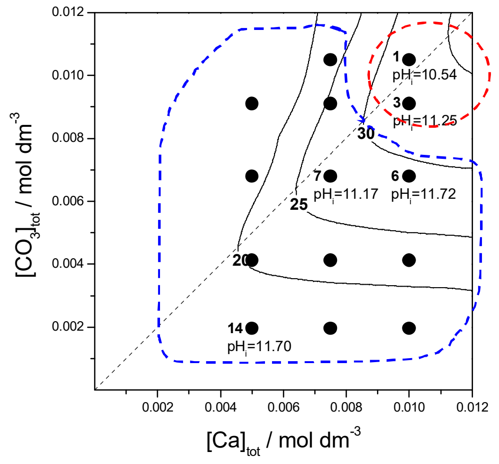
3-D precipitation diagram (precipitation body)



CALCITE + VATERITE

CALCITE

2-D precipitation diagram



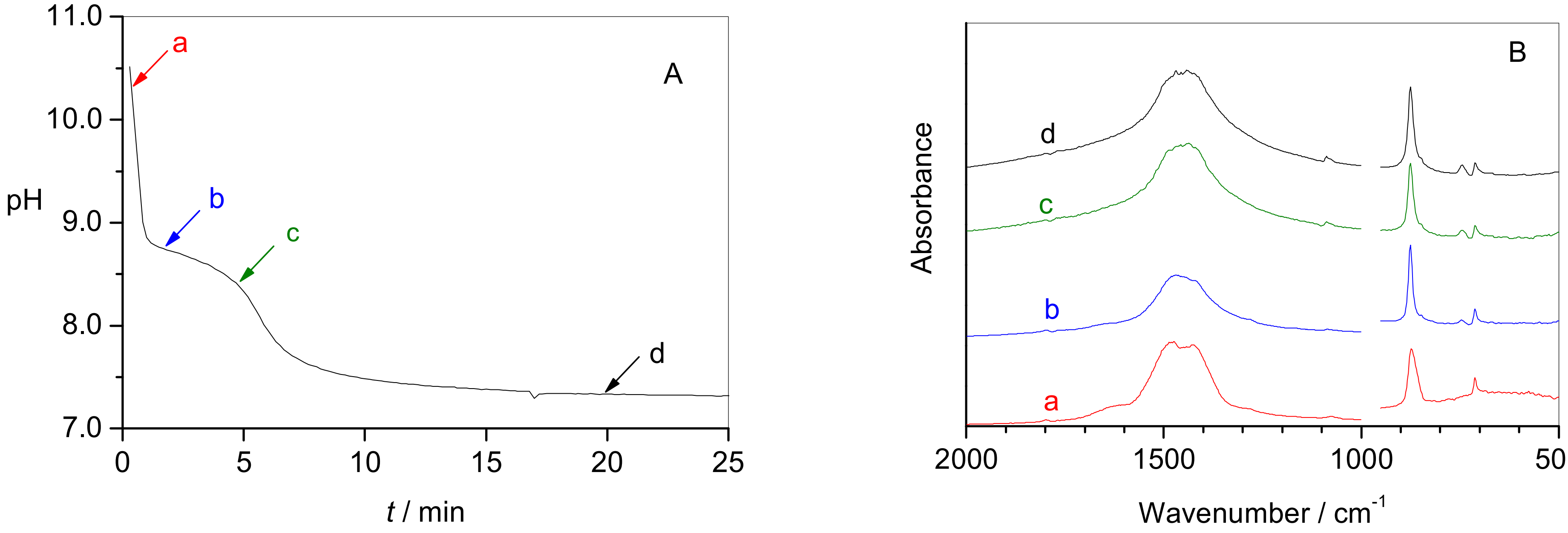
CALCITE + VATERITE

CALCITE

B. Kinetics and mechanisms

a. High initial supersaturation → formation of precursors

Amorphous $CaCO_3$ (a-b) → Vaterite (b-c) → Calcite (c-d)



Role of additives / impurities on relevant properties of calcite

(**Mg^{2+},** Cl^-, NO_3^-, SO_4^{2-})

Facts about role of Mg^{2+} in $CaCO_3$ precipitation

- Mg^{2+} often appear simultaneously with Ca^{2+} (seawater!!)
- Mg^{2+} effective inhibitor of $CaCO_3$ nucleation and growth
- Mg^{2+} initiate precipitation of aragonite
- Readily incorporate into calcite crystal lattice (Mg calcite!!)

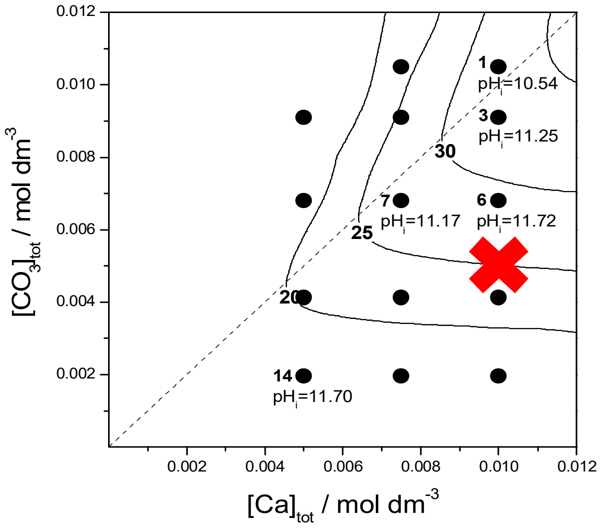
Model system

$c_i(Ca^{2+})$ = 0.01 mol dm^{-3}, $c_i(CO_3^{2-})$ = 0.005 mol dm^{-3}, t = 20 min

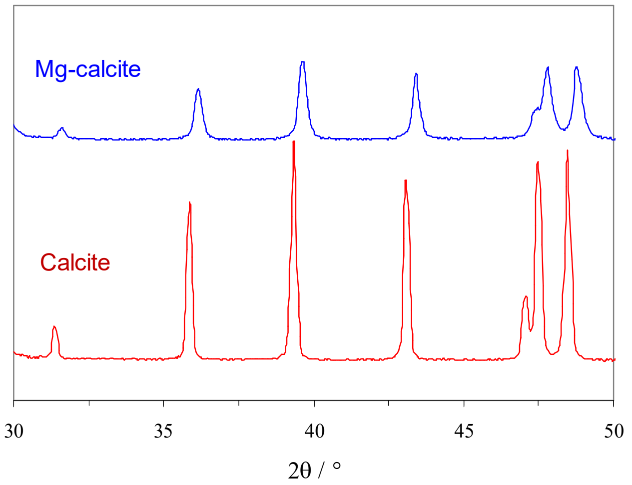
0.001 mol dm^{-3} < $c_i(Mg^{2+})$ < 0.020 mol dm^{-3}

- Initially precipitate calcite – absence of Mg^{2+}
- No precursor - slow precipitation – crystal growth dominant over nucleation
- pH < 9.45 (no $Mg(OH)_2$ coprecipitation)

Precipitation diagram

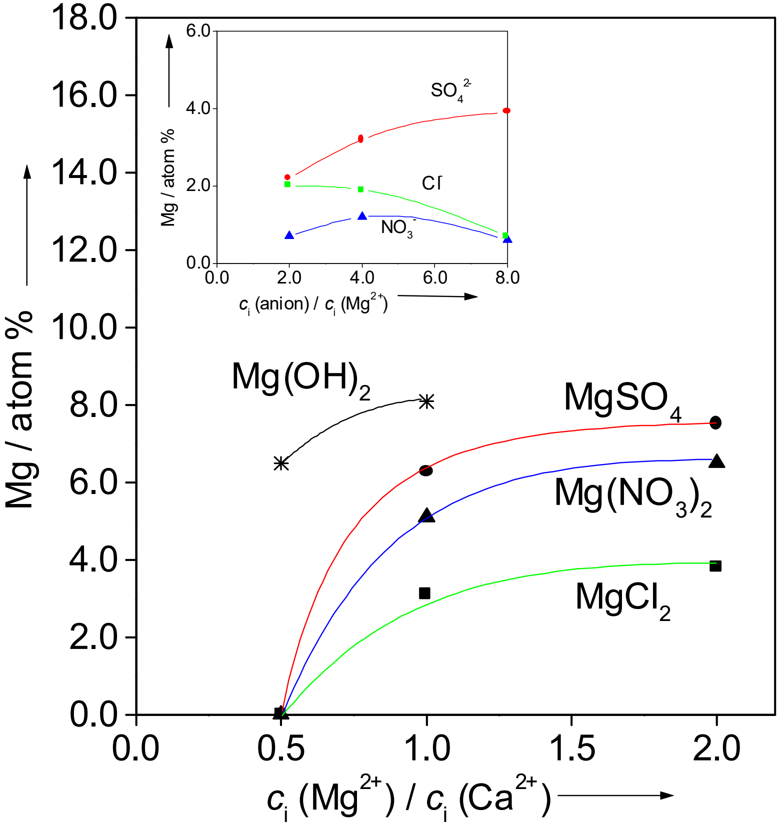


Mineralogical characterization PXRD



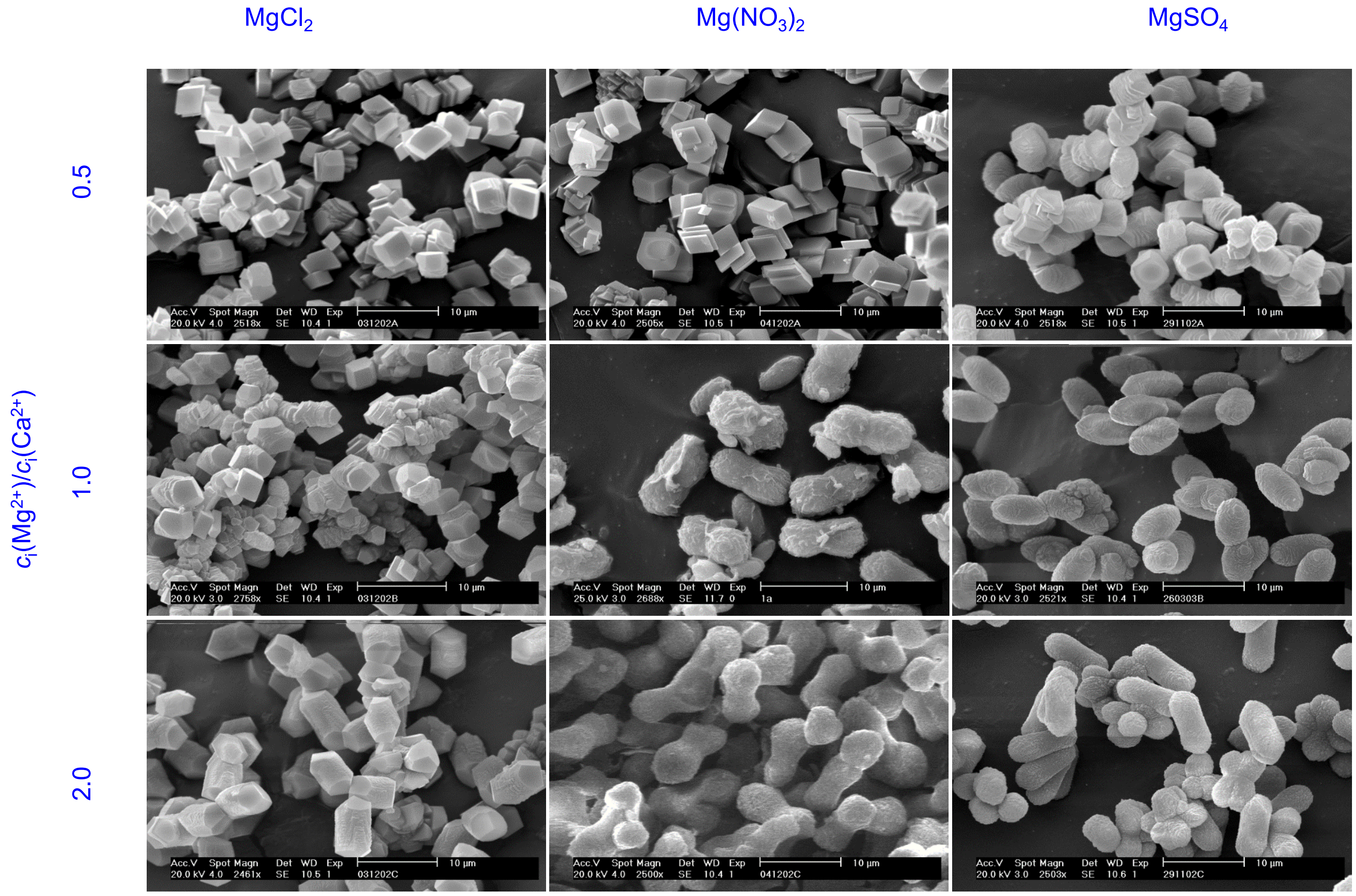
Chemical composition

Mg^{2+} incorporation into calcite crystal lattice



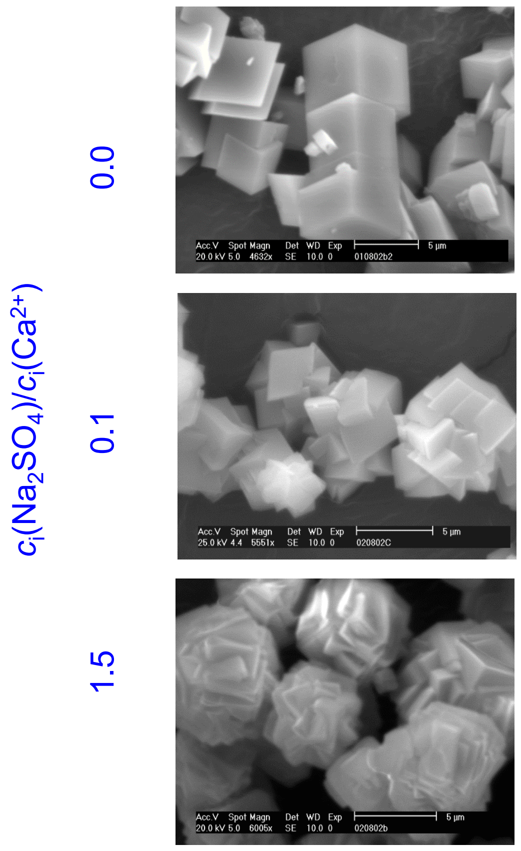
Morphology

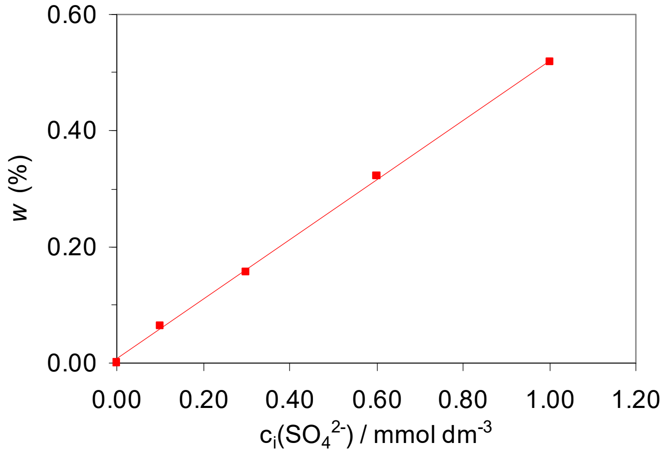
Different Mg^{2+} salts



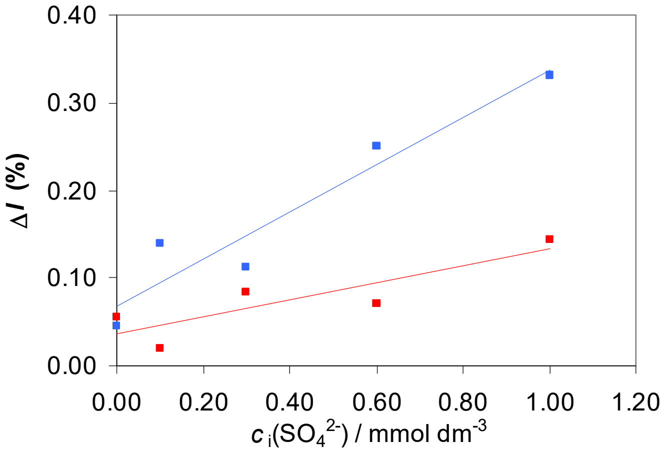
Chemical composition and morphology

SO_4^{2-} incorporation into calcite crystal lattice



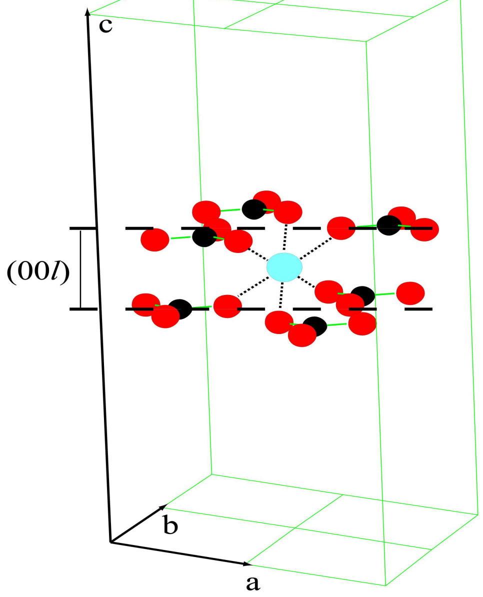


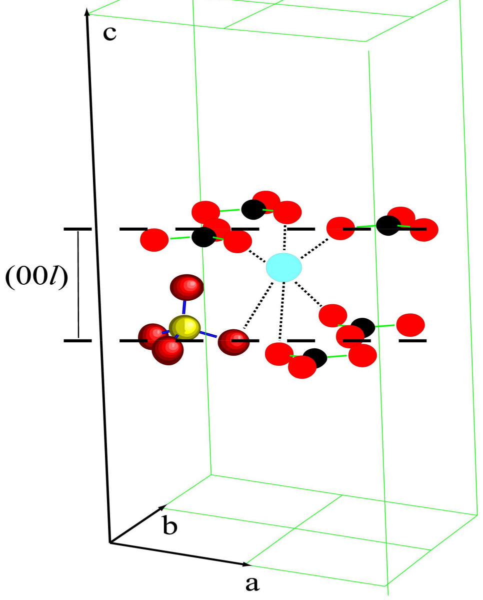
SO_4^{2-} content in calcite



Relative change of crystal lattice parameters (a, c)

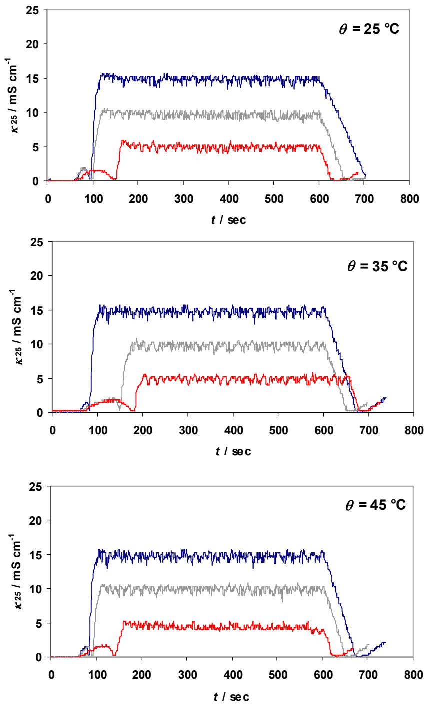
Model of SO_4^{2-} substitution into calcite

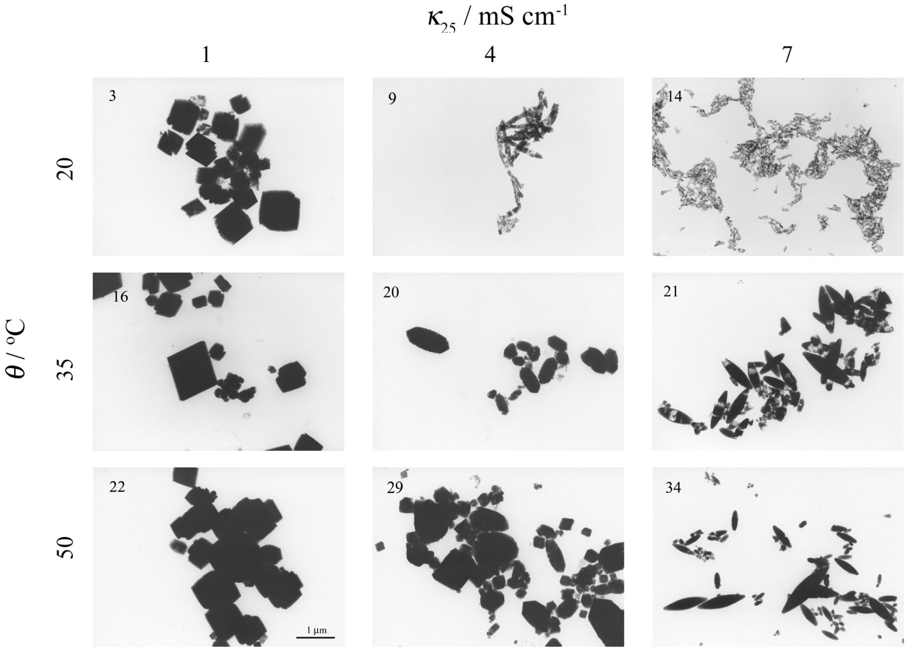




Hydrodynamics

Precipitation at constant composition and temperature





Conclusions

- Precipitation system **$Ca(OH)_2(\mathit{l})$-$H_2CO_3(\mathit{l})$-H_2O** – optimal model for investigation of incorporation of inorganic additives
- Higher supersaturation: precursor phases in mixture with calcite
- Extent of Mg $^{2+}$ incorporation proportional to concentration of respective salt
- Extent of Mg $^{2+}$ incorporation depend on co-anion: increase $MgCl_2 > Mg(NO_3)_2 > MgSO_4$
- Most Mg^{2+} incorporated when no anion, $Mg(OH)_2$
- Isomorphic substitution of Ca^{2+} with Mg $^{2+}$
- Lattice distortion caused by anion increase: $SO_4^{2-} > H_2O > Mg^{2+}$
- Control of Mg-calcite morphology corelated with content of incorporated Mg^{2+} and anions

Research 2

Tufa formation

Precipitation in karst water – monitoring and prevention anthropogenic impact

Facts

Tufa – porous limestone formed by precipitation in karst water at ambient temperature
Travertine – precipitation at elevated temperatures
Tufa formation – either in fluvial channels or lakes

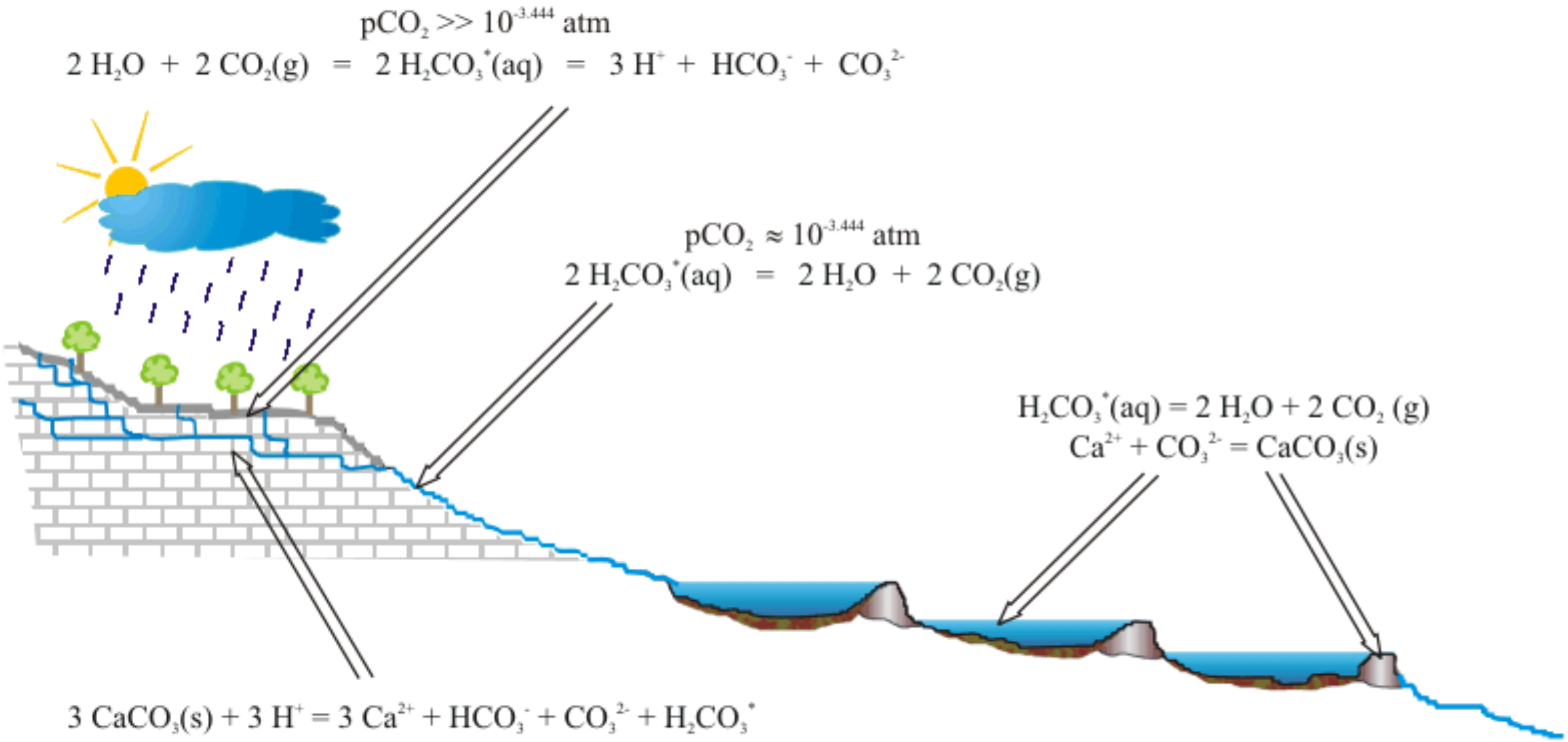
Fluvial tufa
Spring – deposits form on emergence from a spring/seep
Braided channel – deposits dominated by oncoids (layered structures formed by cyanobacterial growth)
Cascade – deposits form at waterfalls (accelerated flow)
Barrage – deposits formed as phytoherm barrages (“freshwater reef”), contain detritus (organic material - leaf, branches etc.

Lacustrine tufa
Formed at lakes’ periphery and built-up phytoherms, stromatolites and oncoids (created by cyanobacteria, sulfate-reducing bacteria or proteobacteria)

Tufa formation endangered by human impact (temperature, increased phosphorous and organic content...)

Specific goals

Determination of the rate of mineralization, Plitvice lakes (Croatia)
Describe process of tufa formation in a context of $CaCO_3$ growth mechanisms
- Supersaturation?
- Substrate?
- **Discern role of natural and anthropogenic inhibitors!**


$pCO_2 >> 10^{-3.444}$ atm
$2\ H_2O + 2\ CO_2(g) = 2\ H_2CO_3^*(aq) = 3\ H^+ + HCO_3^- + CO_3^{2-}$
$pCO_2 \approx 10^{-3.444}$ atm
$2\ H_2CO_3^*(aq) = 2\ H_2O + 2\ CO_2(g)$
$H_2CO_3^*(aq) = 2\ H_2O + 2\ CO_2\ (g)$
$Ca^{2+} + CO_3^{2-} = CaCO_3(s)$
$3\ CaCO_3(s) + 3\ H^+ = 3\ Ca^{2+} + HCO_3^- + CO_3^{2-} + H_2CO_3^*$

Typical karst water composition

		Plitvice lakes (Croatia)	
Ions		c_i(nat) mmol dm^{-3}	c_i(syn) mmol dm^{-3}
Na^+		0,043	0,043
Ca^{2+}		1,520	1,520
Mg^{2+}		0,910	0,910
K^+		0,015	0,015
S $\lvert c_i z_i \rvert$			
Cl^-		0,034	0,034
NO_3^-		0,00	0,00
SO_4^{2-}		0,020	0,010
$H_2PO_4^-$		-	-
HCO_3^-		4,770	4,484
$\Sigma \lvert c_i z_i \rvert$			
	pH	8,24	8,80
		(21 ºC)	(25 ºC)

Calculation of ionic species distribution

Relevant ionic species:

H^+, OH^-, Ca^{2+}, $CaCO_3^0$, $CaHCO_3^+$, $CaSO_4^0$, H_2CO_3*, HCO_3^-, CO_3^{2-},

Mg^{2+}, $MgCO_3^0$, $MgHCO_3^+$, $MgSO_4^0$, SO_4^{2-}, Cl^-, NO_3^-, Na^+, K^+

Initial conditions:

pCO_2, $[Ca]_{tot}$, $[Mg]_{tot}$, $[Na]_{tot}$, $[K]_{tot}$, $[SO_4]_{tot}$, $[Cl]_{tot}$, $[NO_3]_{tot}$

Measurements:

pH (Ca^{2+}, CO_3^{2-})

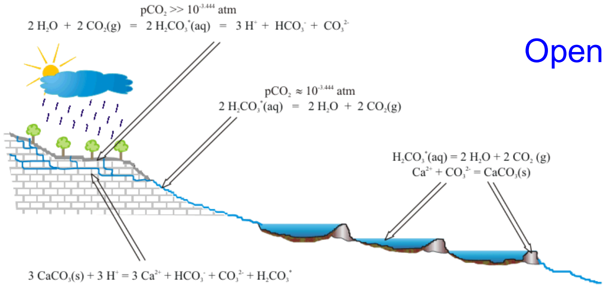
CRITICAL STEP (!!)

Selection of experimental set-up

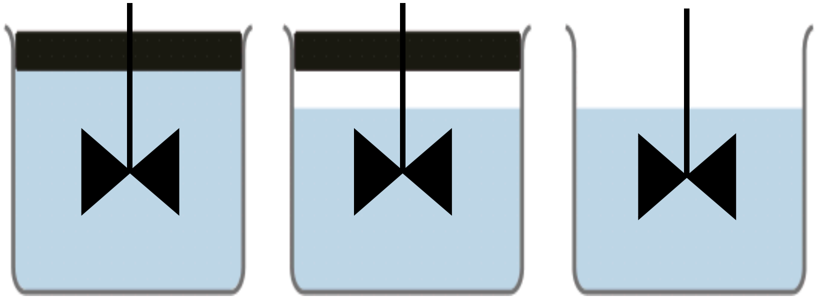
Henry's law (gas law) - the amount of dissolved gas in a liquid is proportional to its partial pressure above the liquid.
Slow equilibration!!!!!!

$$k_H = \frac{[CO_2]_{aq}}{[CO_2]_g}$$

Necessary measurements	Closed system	Semi-closed system	Open system
pH	X	X	X
$[Ca]_{tot}$		X	X
$[CO_3]_{tot}$			X



Open system



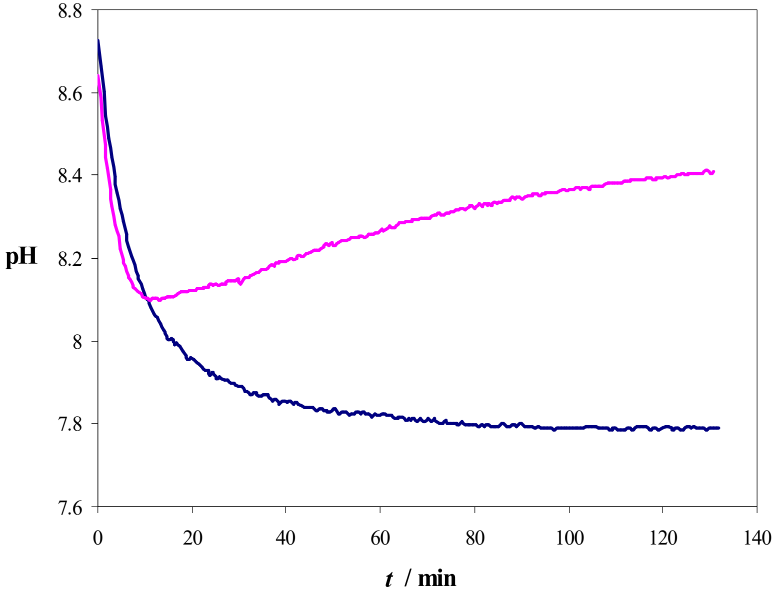
pH measurements in closed *vs*. open precipitation system

$V_o = Vc$

$m_{otv.} = m_{zatv.}$

$Ca^{2+} + HCO_3^- \leftrightarrow CaCO_3(s) + H^+$ *(pH decrease)*

$CO_2(g) \leftrightarrow CO_2(aq) + H_2O \leftrightarrow HCO_3^-(aq) + OH^-$ *(pH increase)*



Simultaneously two processes change the pH:

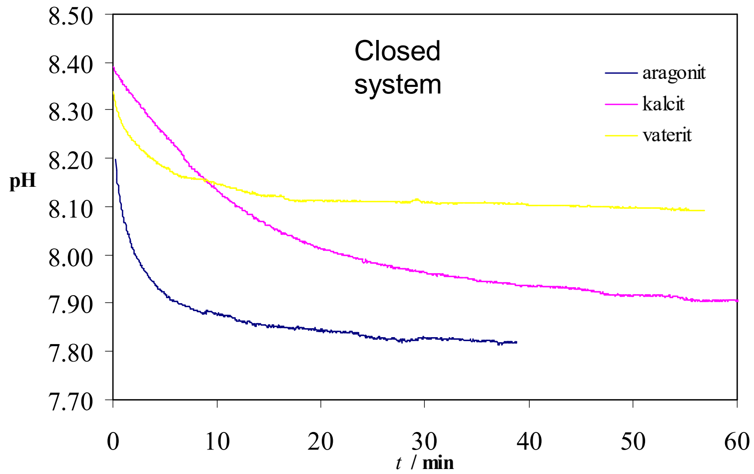
calcite crystal growth (pH decrease)
+
CO_2 degassing (pH increase)

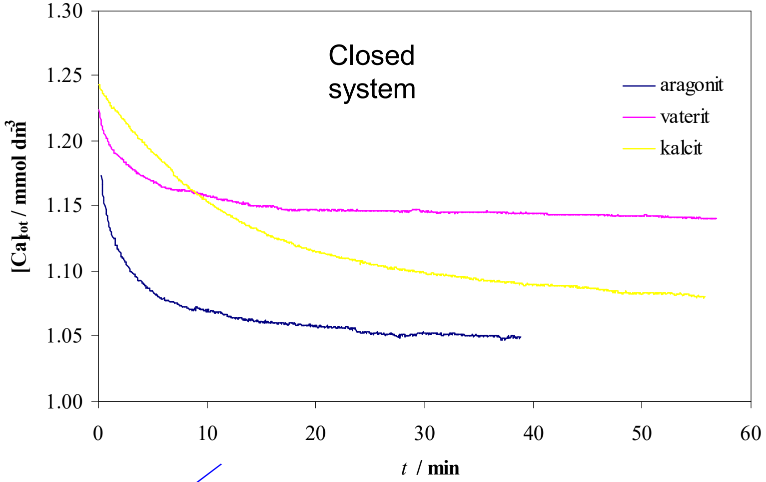
Only calcite crystal growth
(pH decrease)

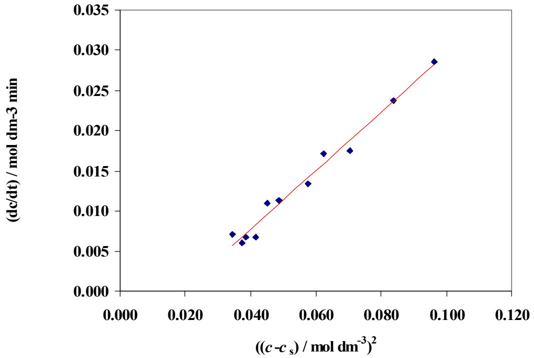
Closed system – growth of different polymorphs

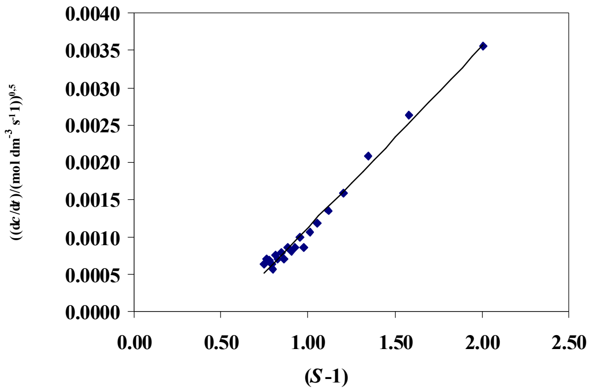
Progress curves (pH vs. time)...

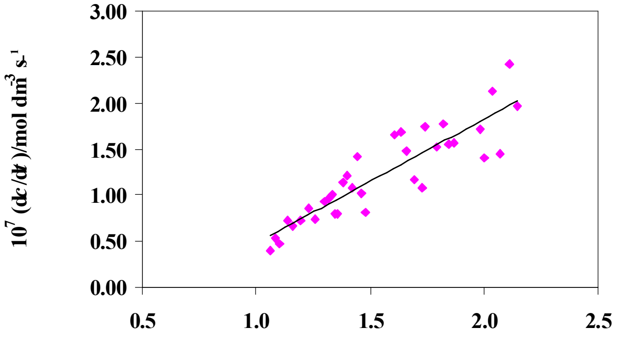
Concentration changes (ctot vs. time)...

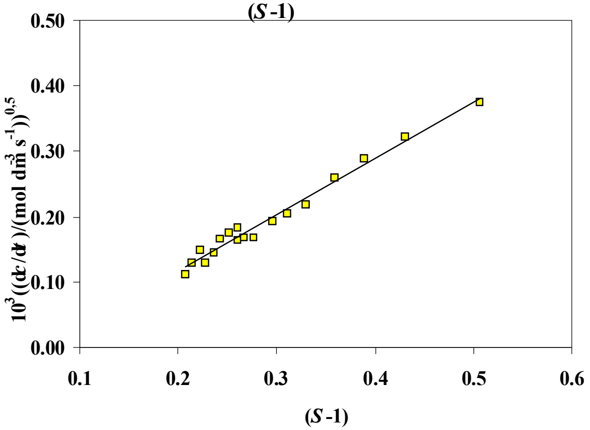












Crystal growth kinetics

↓

Growth Mechanism

Analyses of crystal growth kinetics

(testing the growth rate mechanism)

$dc/dt = -\,k\,A\,(c-c_s)^n$

$n \approx 2$ → (growth on spiral dislocation, low saturation)

(Mg^{2+} incorporation only in calcite!!!)

.

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Research 3

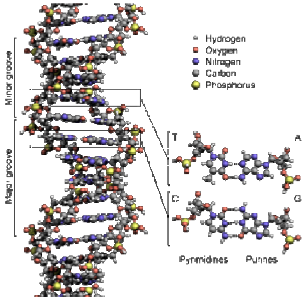
Phosphorous and Environmental Protection

Municipal and Technological Wastewater treatment:
Precipitation or Crystallization ??

Phosphorous

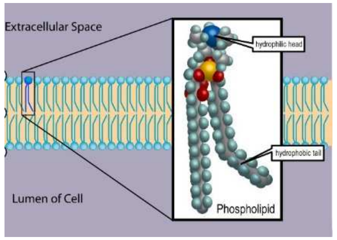
Essential for living world

Organic molecules: DNA, RNA, ATP, phospholipids
Inorganic – biomineralization of bones and teeth; pathological mineralization



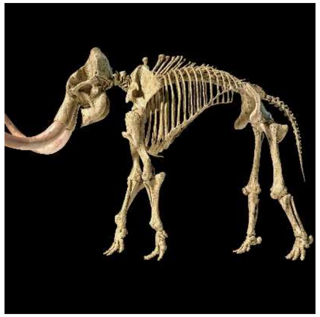
Essential nutrient for plants and animals

Limiting nutrient for aquatic organisms
Over-enrichment of P in fresh waters → algae blooms → eutrophication.



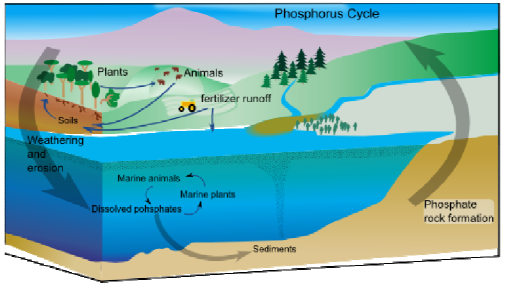
Technological importance

80% the total amount - production of fertilizers
additives in the food industry and production detergents



Geochemical cycle

Transitions P from living world to mineral deposits → about 10-15 M y
One of the slowest biogeochemical cycles
Move quickly through plants and animals;
Move slowly through soil or ocean



http://en.wikipedia.org/wiki/

Apatite - major mineral $Ca_{10}(PO_4)_6(F, Cl, OH)_2$

Limited mineral resources 50 – 200 years ???

Global P stocks Unevenly distributed (80% of stocks in Morocco, China, USA, S. Africa

Eu critical raw material

2014 - EU Commission included phosphate ores in the list of 20 raw materials critical due to their economic importance and supply risk. (http://europa.eu/rapid/press-release_MEMO-14-377_en.htm)

Circular Economy

The Sixth Environment Action Programme of the European Community, “Environment 2010: Our Future, Our Choice”

... Natural resources and wastes are considered as priorities in order to contribute to sustainable development, which is a key feature of policy making in the European Union...”

... Reduction of volume of wastes...

... Recovery of waste streams...

Industrial waste water treatment

Simultaneous phosphorus and fluoride recovery by precipitation/crystallization with Mg^{2+} and NH_4^+

Phosphate rock in phosphoric acid production

Fluoropatite $Ca_{10}(PO_4)_6(F,OH)_2$
Francolite $Ca_{10}(PO_4)_{6-x}(CO_3)_x(F,OH)_{2+X}$

Technology: digestion with sulfuric acid

$$Ca_{10}(PO_4)_6(F,OH)_2 + 3\ H_2SO_4 \rightarrow 2\ H_3PO_4 + 3\ CaSO_4\ (s) + F^- + (...)$$

Waste streams

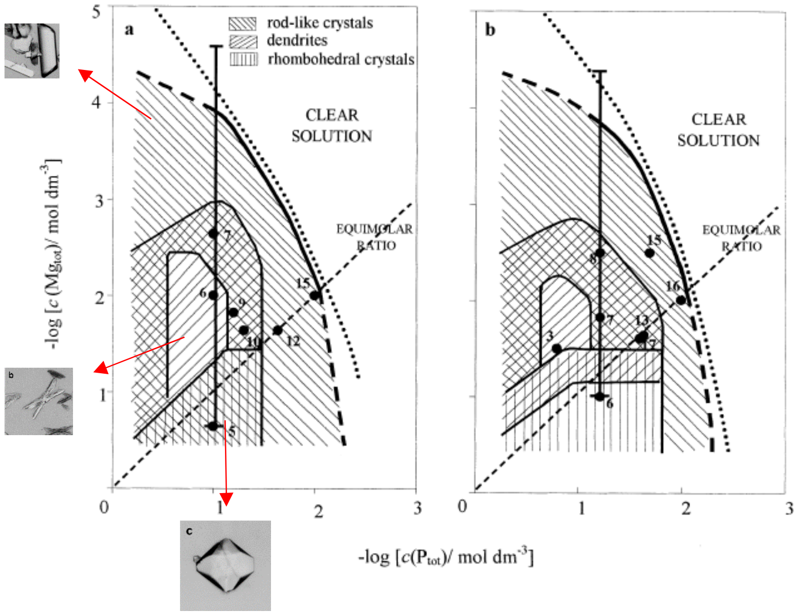
H^+, $H_3PO_4 + 3\ CaSO_4\ (s) + F^-$

!!!!!!
CaF_2 (Fluorite) .... 50 years

A. Phase diagram

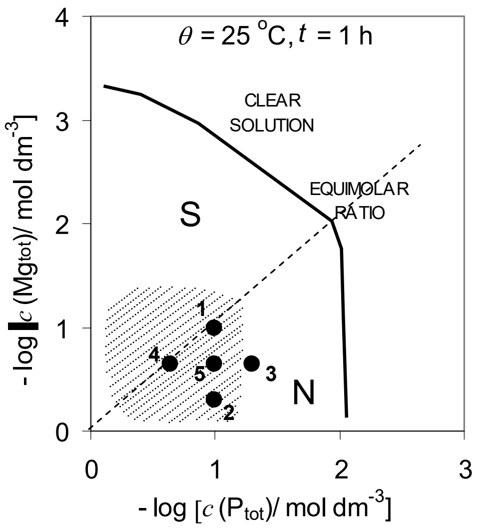
Precipitation system

$MgSO_4$-$NH_4H_2PO_4$-NaCl-H_2O

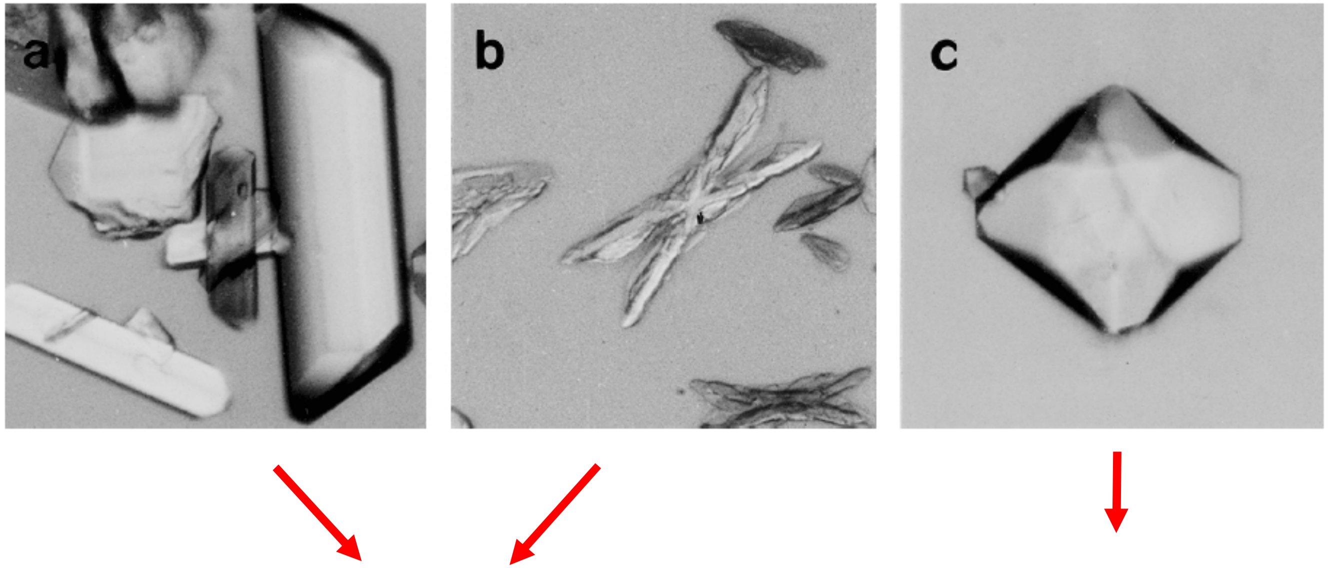


Precipitation system

$MgCl_2$ - $NH_4H_2PO_4$ – NaOH - H_2O



Chemical and structural characterization



struvite ($MgNH_4PO_4 \cdot 6H_2O$)

Newberyrite ($MgHPO_4 \cdot 3H_2O$)

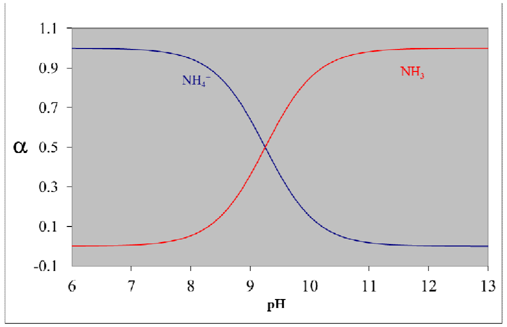
B. Kinetics and crystal growth mechanisms

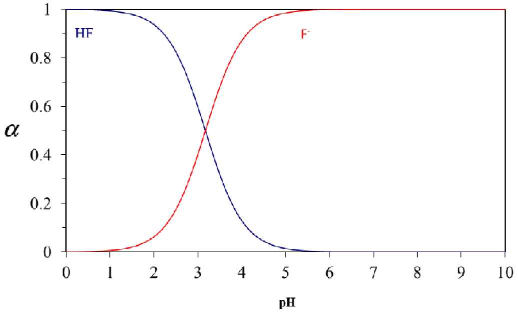
TYPICAL SYNTHETIC TECHNOLOGICAL WASTE WATER COMPOSITION
(major components)

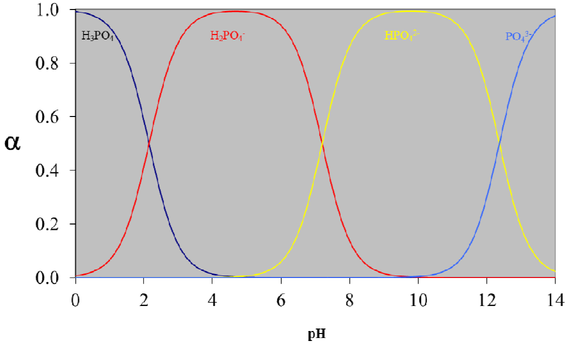
$c\ (PO_4^{3-}) = 0.020\ \text{mol dm}^{-3} \equiv 1000\ \text{ppm}$
$c\ (F^-) = 0.100\ \text{mol dm}^{-3} \equiv 2000\ \text{ppm}$
$c\ (SO_4^{2-}) = 0.009\ \text{mol dm}^{-3}$
$c\ (Ca^{2+}) = 0.002\ \text{mol dm}^{-3}$

pH = 1.85

REMOVAL AND RECOVERY OF IMPURITIES BY PRECIPITATION AS Mg-NH_4 SALT
($8 \le pH_i \le 11$) adjustment with NH_4OH or KOH







STEP 0
(pH adjustment with NaOH)

Protolytic equilibria

H^+ , OH^-

H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}

HF, F^-

Multiple precipitation equilibria
(different chemical and mineralogical products)

$xMg^{2+} + yH_n(PO_4)_m + zNH_4^+ \leftrightarrow Mg_x(NH_4)_z(PO_4)_y$

$Ca^{2+} + H_n(PO_4)_n \leftrightarrow Ca_x(PO_4)_y$

$Ca^{2+} + F^- \leftrightarrow CaF_2$

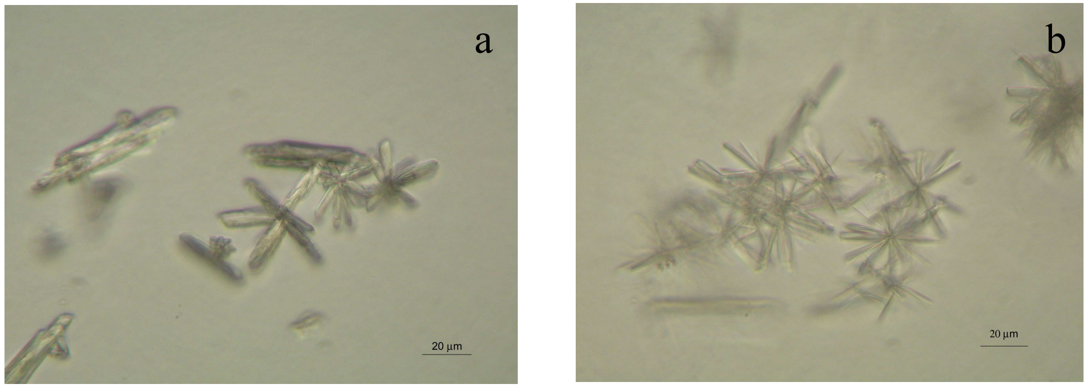
$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$

...

$c\ (PO_4^{3-}) = 0.020$ mol dm^{-3}
$c\ (F^-) = 0.100$ mol dm^{-3}
$c\ (SO_4^{2-}) = 0.009$ mol dm^{-3}
$c\ (Ca^{2+}) = 0.002$ mol dm^{-3}

pH = 1.85

$pH_i = 10$ → Simultaneous fluoride and phosphate precipitation

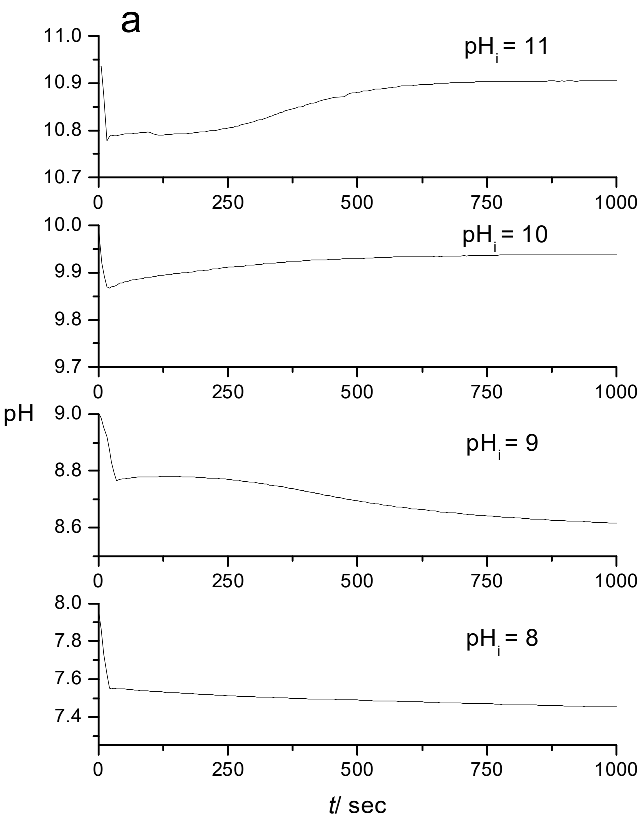


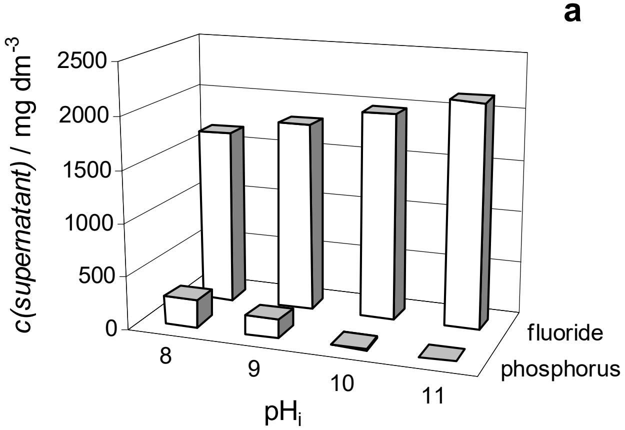
$MgNH_4PO_4 \cdot 6H_2O + MgF_2$, CaF_2

STEP I: phosphate removal **(STRUVITE)**

synthetic waste water + ($MgCl_2$ - NH_4OH)

$PO_4^{3-} + F^- + Mg^{2+} + NH_4^+ + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O(s) + F^-$

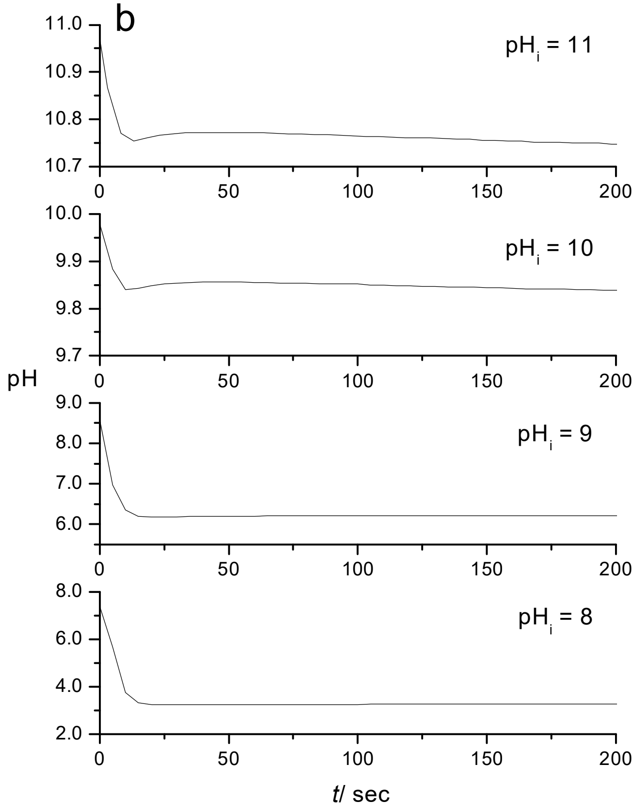




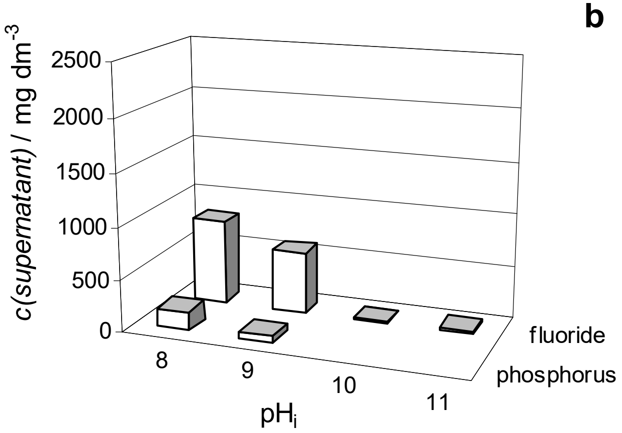
STEP II: fluoride removal (FLUORITE)

synthetic waste water after STEP I + ($CaCl_2$ - NH_4OH)

$PO_4^{3-} + F^- + Ca^{2+} + NH_4^+ \rightarrow CaF_2(s) + Ca_3(PO_4)_2(s)$



Waste water after treatment



STEP I: *c* (F^-) ≈ 1500 mg dm^{-3} , *c* (PO_4^{3-}) ≈ 4 mg dm^{-3}

STEP II: *c* (F^-) < 9 mg dm^{-3}, *c* (PO_4^{3-}) < 0,1 mg dm^{-3}

Allowed to dispose in water bodies:

c (PO_4^{3-}) = 2 mg dm^{-3}
c (F^-) = 8 mg dm^{-3}

Major by-products (circular economy!!)
Struvite - ecologically acceptable slow release Mg-N-P fertilizer, ≈1000 USD /T
Fluorite - CaF_2

Future research

Phosphorus recovery from municipal waste waters

Crystallization or Precipitation????

Municipal waste water treatment plants

(High levels of nitrogen and phosphorous)

Preliminary treatment

Coarse material removal by screening (inorganic particles greater than 0.210 mm)

Primary treatment

Removal of a portion of the suspended solids and organic matter from the sewage
Removal 50-70% of the suspended solids and 25-40% of the biological oxygen demand (BOD)

Secondary treatment

Removal of biodegradable organic matter (in solution or suspension) from sewage
Biological processes used to remove dissolved and suspended organic matter
Microorganisms in a sequenced aerobic or anaerobic process

Tertiary treatment

Advanced sewage treatment - final treatment stage to further improve the effluent quality before it is discharged or reused
Several tertiary treatment process may be used at any treatment plant
Tertiary treatment - may include **biological nutrient removal**, **disinfection** and removal of **micropollutants** (pharmaceuticals...)

Secondary treatment - Biological nutrient removal

Nitrogen removal by nitrification + denitrification

$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^- \rightarrow N_2$

Typical values in raw sewage:

6-10 g/person/d for **total nitrogen** (35-60 mg/L)

3.5-6 g/person/d for **ammonia-N** (20-35 mg/L)

Phosphorus removal

Limiting nutrient for algae growth in many fresh water systems - eutrophication

F**ouling of downstream equipment** such as reverse osmosis.

Typical values: 0.7-2.5 g/person/d for total phosphorus (4-15 mg/L)

Enhanced biological phosphorus removal (EBPR) – two step process

$PO_4^{3-} \rightarrow OH(PO_3)_nH \rightarrow PO_4^{3-}$

Aerobic conditions: polyphosphate-accumulating organisms (PAO, Accumulibacter)) take phosphorus and store as polyphosphate

Anaerobic conditions: bacteria metabolize the polyphosphate and release orthophosphate into solution

Disposal

Chemical process 1

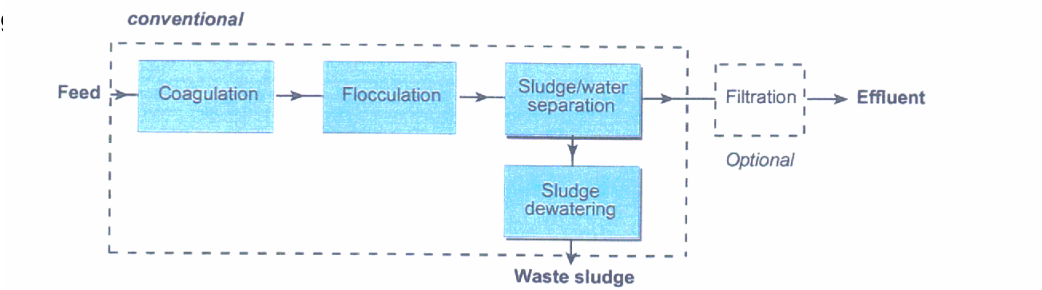
Precipitation of phosphate at initial stage of water treatment

Precipitation by using **ferric chloride**, **alum** and/or **lime**

Floculation caused excessive sludge production as hydroxides (water 60 - 80 %)

Expensive chemicals, dfficult separation

Several technolo



Chemical process 2

Crystallization during the EBPR process (anaerobic stage)

Chemistry - identical to precipitation process: $3Me^{2+} + 2PO_4^{3-} + nH_2O = Me_3(PO_4)_2 \cdot nH_2O$

Different products possible: apatites, Mg-phospates, Mg-NH4-phosphates...

Inoculation by inorganic seed material - controll the supersaturation (low S) → CRYSTALLIZATION

Low water content (1 - 5 %) and large pellets (0.8 – 1.0 mm)

Chemically pure pellets (90 – 98 % phosphate) - recycling or direct use as commercial product

No co-crystallization of impurities (heavy metals)

Low P in effluent (Ksp of different phosphate salts)

Multiple imapacts of phosphorous crystallization:

Struvite - ecologically acceptable slow release Mg-N-P fertilizer (≈ 1000 USD / T);
Low operational cost - 5 - 7 USD / kg P
Low amount of solid waste;
Complementary to present technologies for waste water treatment
Lowering the maintenance costs – prevention of incrustation