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

Teaching week 2025

Crystallization in biomineralization and in the environment

1. Kinetics and Mechanisms of Precipitation (Crystallization) Processes

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Crystallization in biomineralization and in the environment

1. Kinetics and Mechanisms of Precipitation (Crystallization) Processes
2. Calcium Carbonates
3. Calcium Carbonates - Model Systems in Biomineralization
4. Calcium Carbonates - Model System in Environment

1. Kinetics and Mechanisms of Precipitation (Crystallization) Processes

Definition of Process

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)

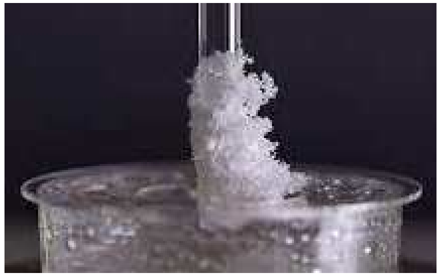
Solid in liquid (crystals in suspension)
(Precipitation in limited sense!!)

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: $Ag^+(aq) + Cl^-(ag) \leftrightarrows AgCl(s)$)

- 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: $2Ag^+(aq) + CrO_4^-(aq) \leftrightarrows Ag_2CrO_4(s)$)

- Solubility = 50.0 mg/L (45 °C)
- Micron-sized particles

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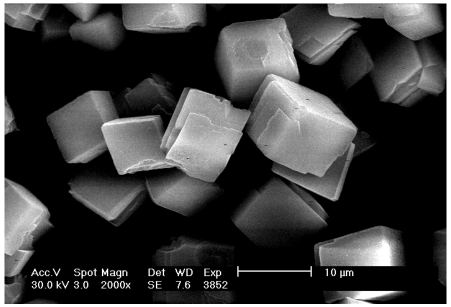
Crystallization and Precipitation - Examples

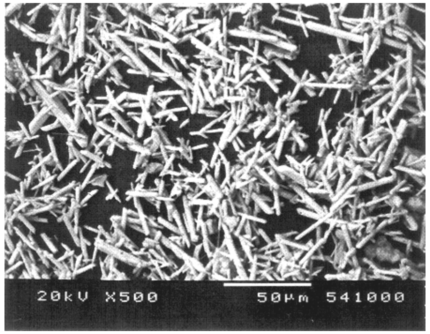
calcite, $CaCO_3$

solubility = 13 mg / L



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 → often soluble salts

Small crystals → less soluble salts

Precipitate → very often crystalline

Some empirical definitions

Precipitation = crystallization of slightly soluble salts

Precipitation = fast crystallization

Crystallization → soluble salts → large crystals

Precipitation → slightly soluble salts → small crystals (colloidal)

PRECIPITATION → MORE GENERAL TERM!

Solubility

Solubility (definition) = the maximum amount of substance that could dissolve in a given volume 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 chlorides, bromides and iodides are soluble.
4. All sulfates are soluble, except calcium sulfate and barium sulfate.
5. All silver, lead and mercury(**I**) salts are insoluble.
6. All carbonates, sulphides, oxides and hydroxides are insoluble (!!!).

Equilibrium in heterogeneous systems of ionic salts

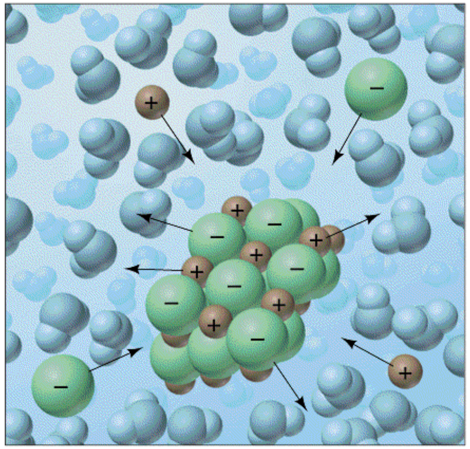
$MA \leftrightharpoons M^+ + A^-$

In saturated solution containing solid phase (suspension) → **dynamic equilibrium**

Dynamic equilibrium: Dissolution rate = Precipitation (crystallization) rate

Solubility product (K_{sp}) of salt MA and reaction: $MA(s) \leftrightharpoons M^+ + A^-$

$$K_{sp} = ([M^+]\cdot[A^-]) / \cancel{[MA]}(s) = [M^+]\cdot[A^-]$$



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

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How to estimate solubility (c_s) from K_{sp}??

K_{sp} – basic thermodynamic property of compound (tables)

Magnesium carbonate ($MgCO_3$)

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

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

Magnesium fluoride (MgF_2)

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

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

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}

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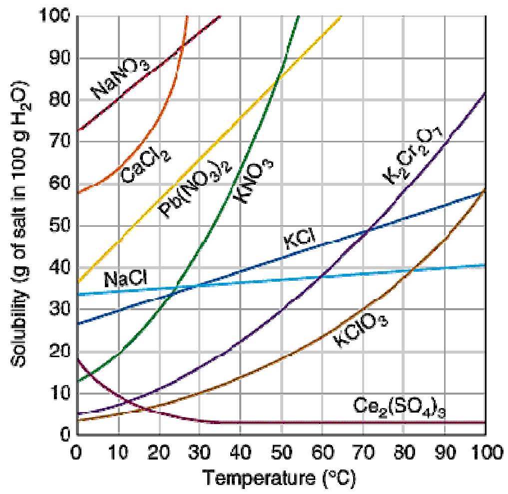
Factors which determine the solubility of ionic salts



Temperature change → Increase of solubility (!)

Complexation of constituent ions → Increase of solubility

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

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

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

Common ion addition → Decrease of solubility

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

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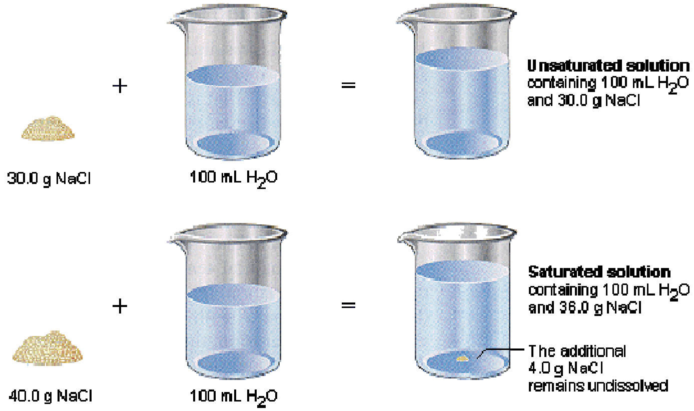
Measure of solution stability



$c = c_s$ saturated solution (no dissolution, no precipitation $\rightarrow$ 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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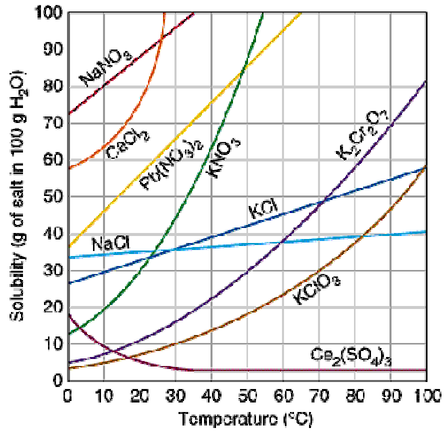
How to initiate precipitation / crystallization??



1. Temperature change (decrease) – very often solubility higher at higher temperatures

2. Evaporation of solvent – change of constituent ion concentration

3. Chemical reaction / mixing the components

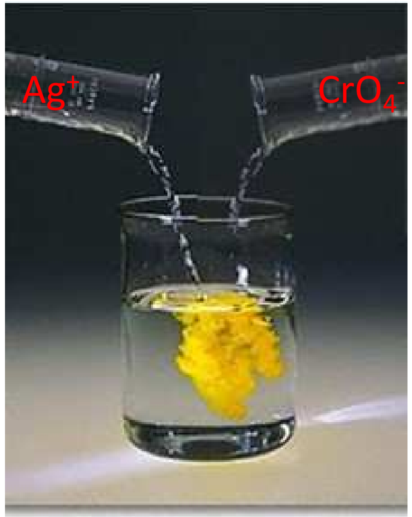
Illustrations from: M. S. Silberberg, Chemistry – The molecular Nature of Matter and Change, Fourth Edition, McGrow-Hill, 2006

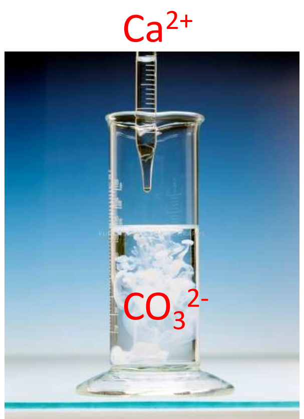
Chemical reaction (mixing the reactants) → suitable for slightly soluble salts (fast)

Soluble salt AX + Soluble salt BY ⇆ **Insoluble salt AB** + Soluble X + Soluble Y

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

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





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

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

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

Importance of investigation of crystallization (precipitation)???

Geology, geochemistry, ocenology

- Formation of sedimentary rocks and minerals
- Sea water buffering: absorption of CO_2 → $CaCO_3$ 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 (materials science)

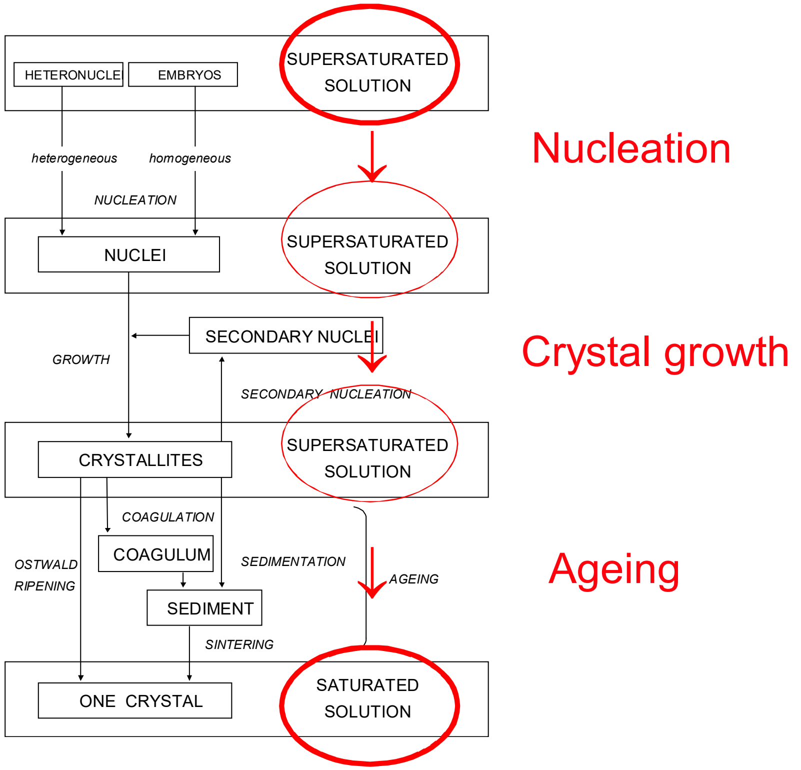
- Biomineralization (bones, teeth, shells, ...), pathological mineralization

Environmental protection....

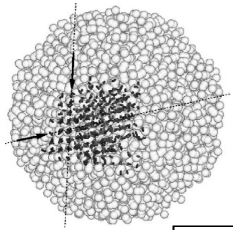
Mechanisms of precipitation (crystallization) processes

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

Precipitation → Stepwise process = Nucleation + Crystal Growth + Ageing



Nucleation



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

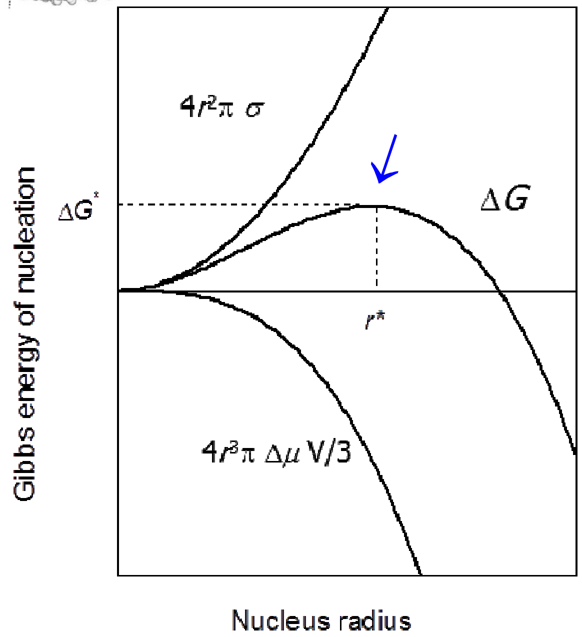
Classical nucleation theory: Critical nucleus (r^*) is a tiny peace of solid phase with all physical chemical properties of macroscopic structure, which stabilize by dissolution or growth

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)
(volume, surface area, surface tension, chem. potential)

$$\Delta G = \Delta G_{Vol} + \Delta G_{Sur}$$
$$\Delta G = V\,\Delta\mu_v + A\,\sigma$$
$$\Delta G = (4r^3\pi/3)\,\Delta\mu_v + 4r^2\pi\,\sigma$$

Empirical discrimination of nucleation mechanisms

(Number of nuclei (crystals) vs. initial supersaturation)

Homogeneous nucleation - by interaction (collision) of constituents

$n \approx 10^7 – 10^{12}$ cm^{-3}

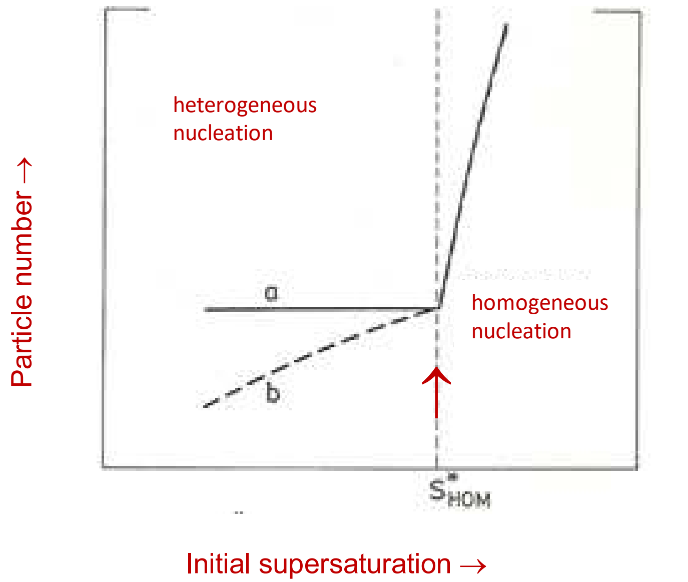
Heterogeneous nucleation – catalyzed by suspended impurities, seeding

$n \approx 10^6 – 10^7$ cm^{-3}

(Water undercooling: - 48.3 °C)

Nucleation rate (J)

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



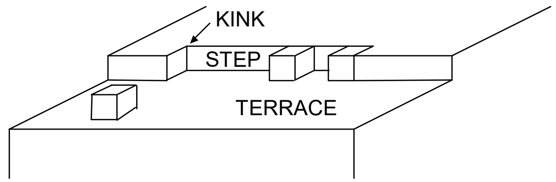
S^*_{HOM} – critical supersaturation for homogeneous nucleation

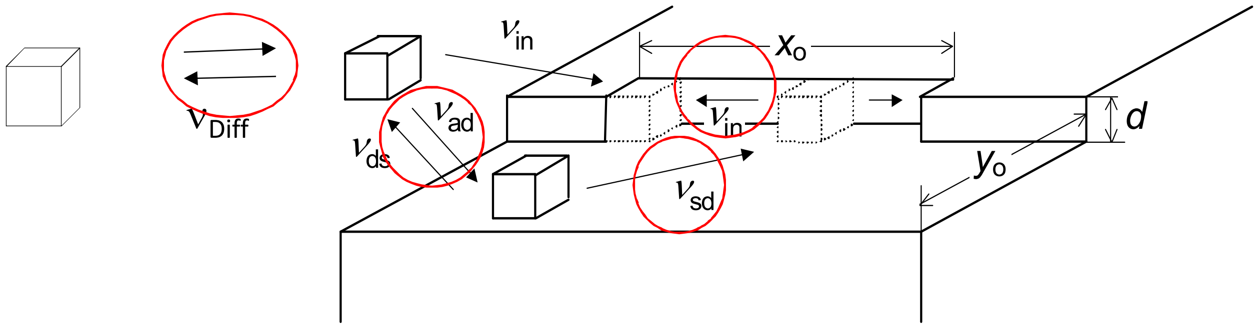
Crystal growth

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

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

Crystal growth $\rightarrow$ consecutive processes $\rightarrow$ slowest control the overall growth
(volume diffusion and convection of ions, adsorption, surface diffusion, edge diffusion, integration into crystal lattice)





Diffusion controlled growth	$rate = D \cdot V_m \cdot (c - c_s)/r$	(linear growth rate low)
Adsorption controlled growth	$rate = (V_m/A)Ad(c\nu_{ad} - AdK_{ad}c_s\nu_{ds}) = V_m d\nu_{ad}c_s(S-1) = k_1(S-1)$	(linear growth rate low)
Surface nucleation controlled growth	$rate = A \cdot \exp(-B/\ln S)$	(exponential growth rate low)
Spiral (dislocation) controlled growth	$rate = k_2 \cdot (S-1) \cdot \ln S \approx dr/dt = k_2 \cdot (S-1)^2$	(parabolic growth rate low)

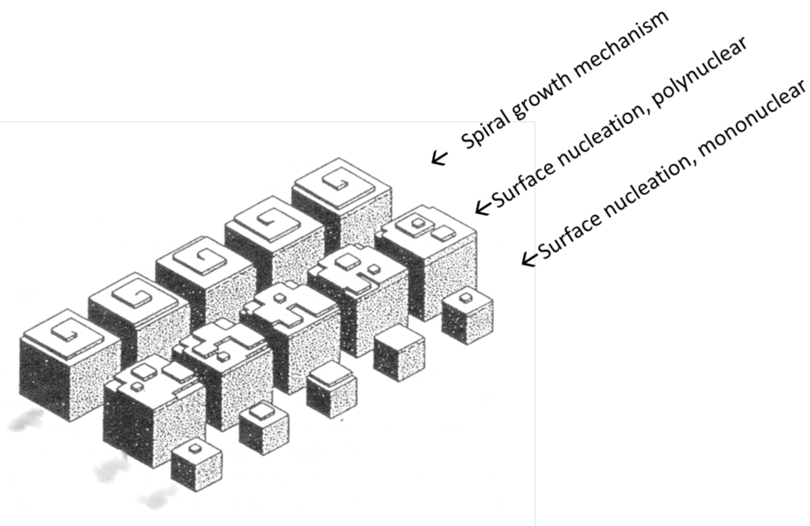
Surface controlled mechanisms (incorporation of constituents into crystal structure)

Surface nucleation controlled growth $rate = A \cdot \exp(-B/\ln S)$ "Exponential growth rate low"

- Steps and kinks emerge by nucleation at the surface (surface islands)
- Growth at high supersaturation!

Spiral (dislocation) controlled growth $rate = k_2 \cdot (S-1) \cdot \ln S \approx k_2 \cdot (S-1)^2$ "Parabolic growth rate low"

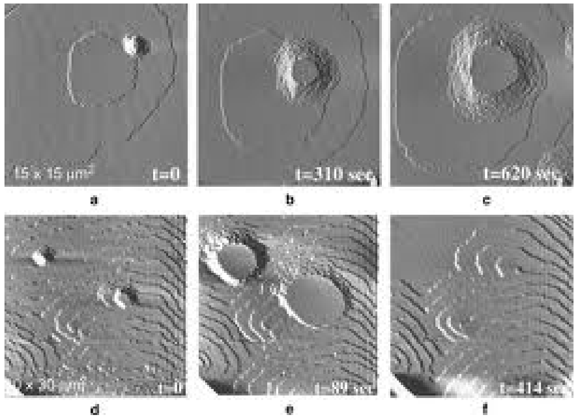
- Steps are present on the crystal surface (surface imperfection – screw dislocation), no need for nucleation
- Growth at extremely low supersaturation!!



Visualization of crystal surfaces during growth in solution

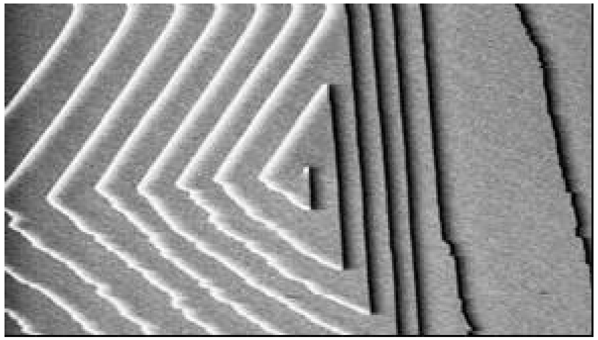
Growth by surface nucleation

$dL/dt = A \cdot \exp(-B/\ln S)$



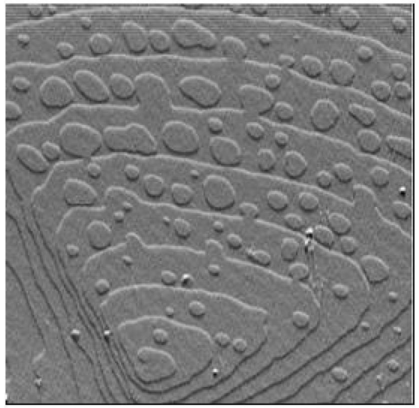
Growth on spiral step

$dL/dt = k_2 \cdot (S-1)^2$

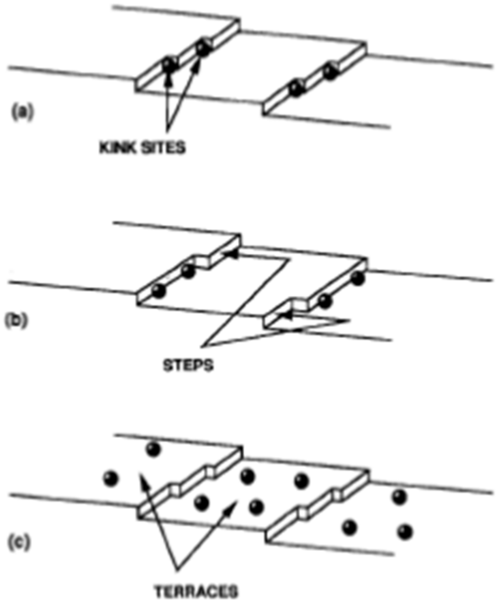


Growth on spiral step + surface nucleation

$dL/dt = k_2 \cdot (S-1)^2 + A \cdot \exp(-B/\ln S)$



Impurities and crystal growth



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

Additive - deliberately added impurity

Impurities in contact with crystallizing compound can 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, solubility...)

Impurities change the crystal morphology !!!!

Impurities change the growth mechanism !!!!

Why to investigate crystal growth kinetics and mechanisms??

1. Precipitation kinetics (kinetic data)

↓

2. Precipitation mechanisms

↓

3. Control of physical-chemical properties of precipitate
(polymorphism, size distribution, morphology, ...)

Critical precipitation parameters:

Initial concentration of reactants (supersaturation)
Reactants' concentration ratio
Temperature
Hydrodynamics
Impurities (additives)

vs.

Critical properties of solid phase:

Structure (polymorphism)
Chemical composition
Size distribution
Morphology

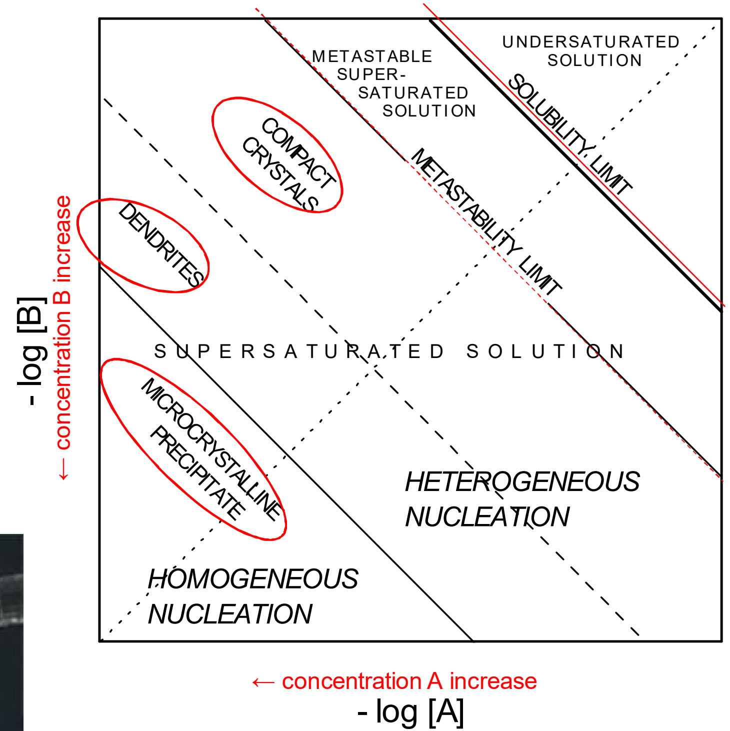
Precipitation processes - research strategy

A. Construction of precipitation (phase) diagrams

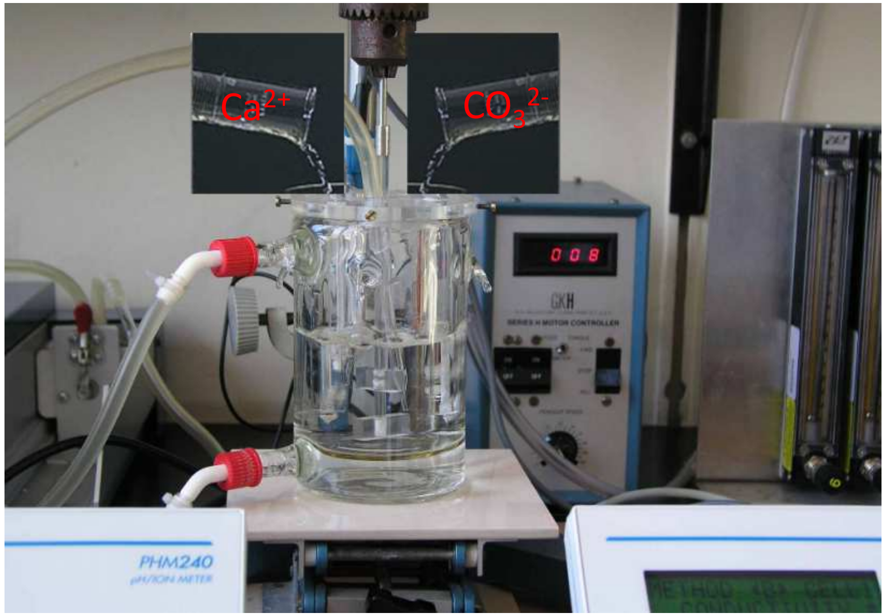
- Precipitation diagram = graphical presentation of precipitation system of slightly soluble salt: $AB \leftrightarrows A^+ + B^-$

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

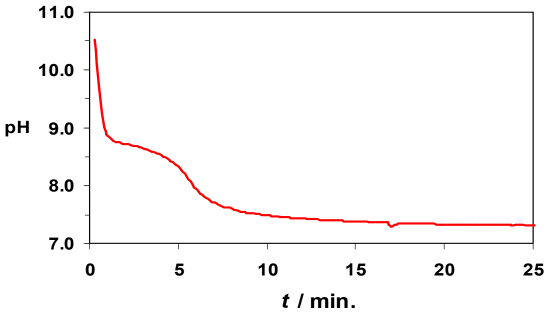
- Isergons – isograms (lines) of constant relative supersaturation (S-1)
- Solubility boundary, (S-1) = 0
- Precipitation boundary (metastability limit)
- Heterogeneous nucleation (growth by inoculation (seeding))
- Solubility < (S-1) < Precipitation boundary
- Homogeneous nucleation (spontaneous precipitation):
- (S-1) >> Precipitation boundary



B. Precipitation kinetics and mechanism



Data acquisition



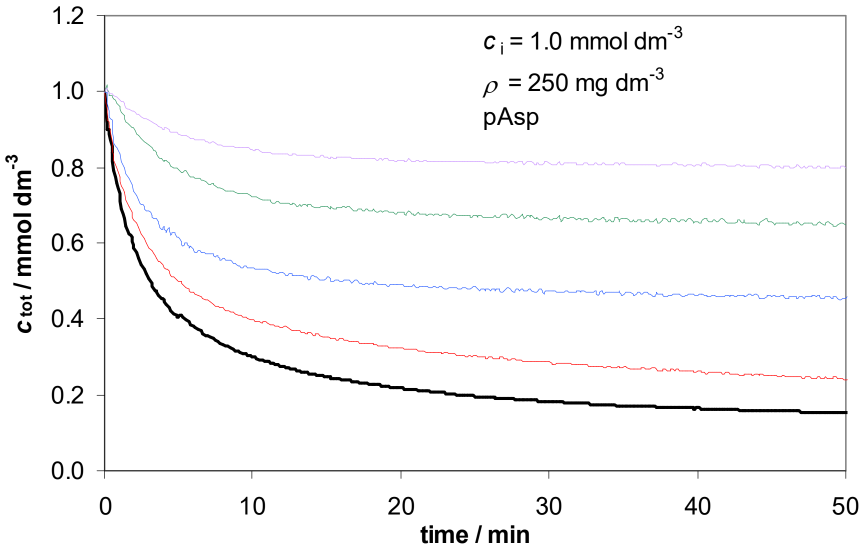
Experimental set-up – measurements of reaction propagation
Beaker + temperature control + stirring
Sensor - progress of reaction (ion selective electrode, pH, conductivity, size distribution, chemical analysis...)

Analysis of growth kinetics

1. Progress curves

$c = f(t)$

$m = f(t)$



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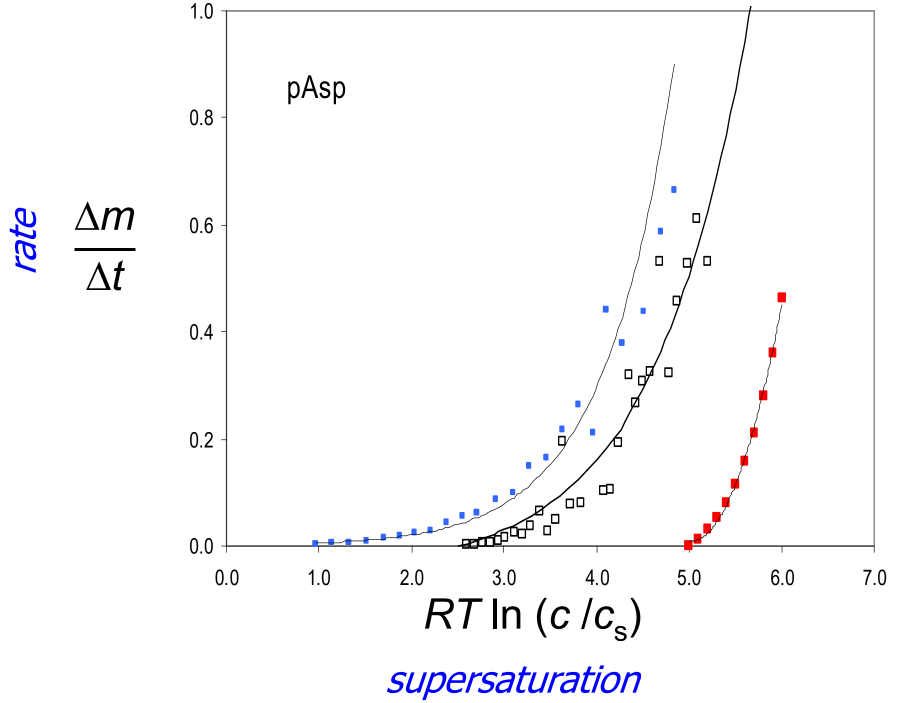
2. Calculation of growth rate and supersaturation

$$Rate = \frac{(c_1 - c_2)}{(t_1 - t_2)} = \frac{\Delta c}{\Delta t} \propto \frac{\Delta m}{\Delta t}$$

Supersaturation = $\phi = RT \ln (c / c_s)$



rate = f (supersaturation)

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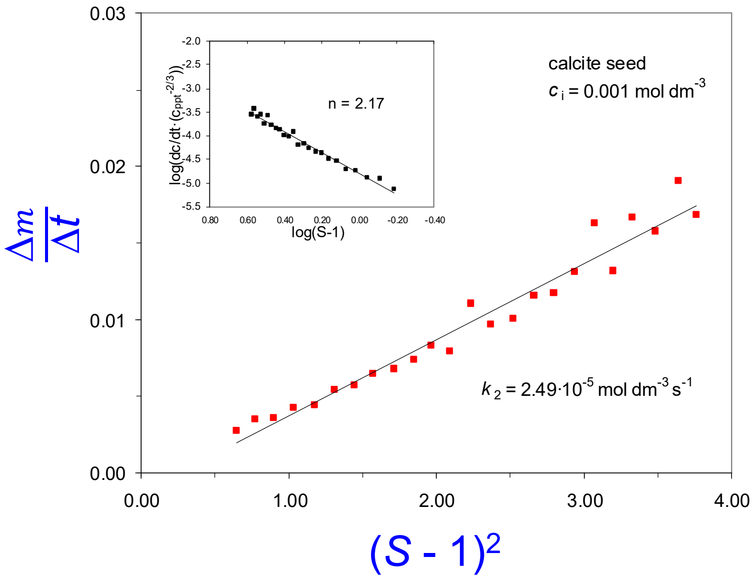
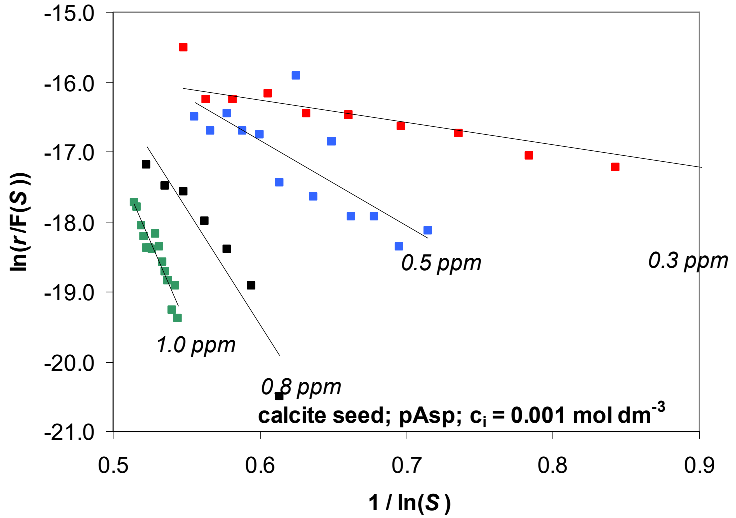
3. Testing the theoretical crystal growth laws (models)





$$rate = \frac{\Delta m}{\Delta t} = k_2 (S - 1)^2$$

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

Parabolic growth rate → Growth on dislocation

Exponential growth rate → Nucleation control

↓

Analytical characterization of solution and solid phase

Morphology (SEM / EDS)

Crystal size distribution (DLS, CC)

Chemical analysis (chromatography, spectroscopy...)

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