Mineralogy

Course of Mineralogy G102
Second Semester (February-June, 2014)
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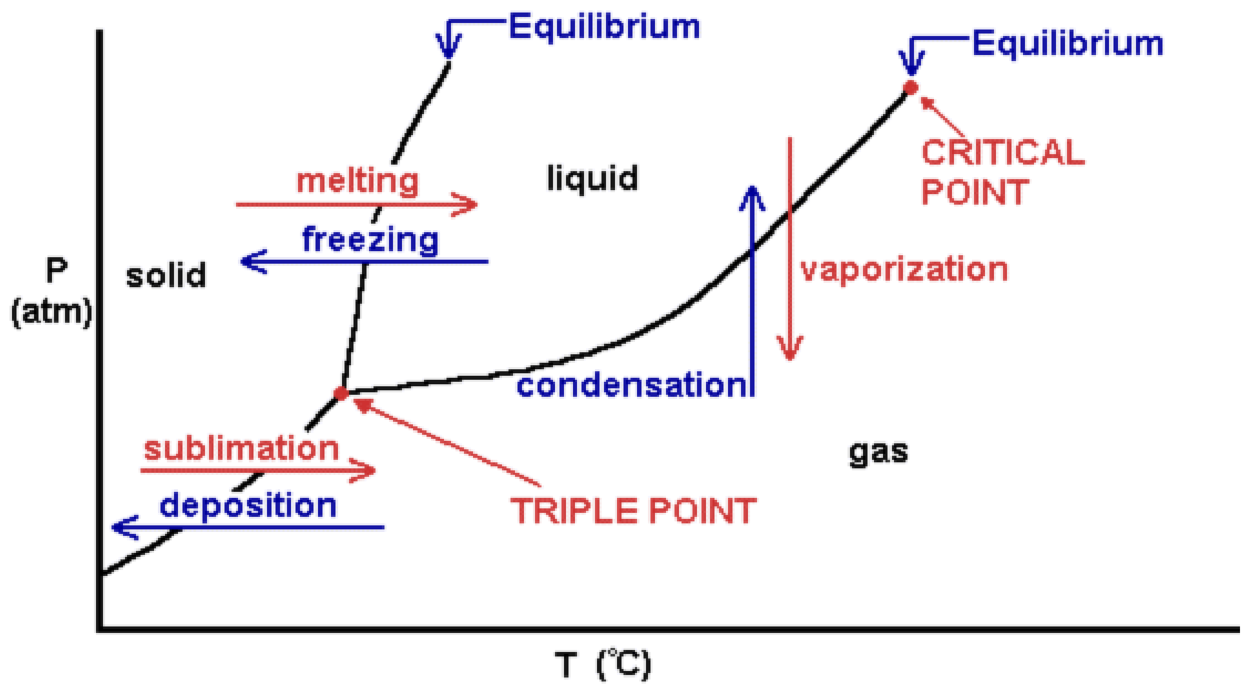
Lecture 3

Crystallization and Dissolution of Minerals

Part 1

Phase transformation

- Phase transformation in geological environments are characterized by:
  - 1- Vaporization
  - 2- Condensation
  - 3- Crystallization
  - 4- Melting
  - 5- Dissolution
  - 6- Sublimation



From www.kentchemistry.com

Note//

- Neither gases nor liquids are likely to be pure in the geological environments. So, they are mixtures, although a particular element or compound may dominate.
- Ex:
  - Nitrogen in air
  - H_2O in hydrothermal and low-temperature aqueous system
  - Silic polymers dominate most magamtic systems

Mineralogical reactions

- Mineral reactions are chemical reactions that involve the destruction or formation or minerals.
- Ex: halite mineral's reaction:
- 1- halite $\longrightarrow$ $Na^{+} + Cl^{-}$ *(dissolution)*
- 2- $Na^{+} + Cl^{-}$ $\longrightarrow$ halite *(precipitation)*
- 3- halite = $Na^{+} + Cl^{-}$ or $Na^{+} + Cl^{-}$ = halite *(an equilibrium state which there is coexistence of halite and saline solution).*
- Note/ chemical equilibrium is rare in geological environments.

- The rates of reactions in aqueous solutions in contact with solids are controlled by:
- 1- the movement of aqueous species to or from the liquid-solid surface by diffusion or advection.
- 2- the rates of bond breakage and bond formation at the interface.

Chemical reaction

Attachment kinetics

(crystal growth)

Detachment kinetics

(crystal dissolution)

Factors controls the chemical reactions:

- 1- temperature: prograde solution, retrograde solution
- 2- pressure
- 3- ionic potential
- 4- ionic activity and ionic strength
- 5- pH (activity of hydrogen ion)
- 6- Eh (oxidation-reduction)

The solid-fluid interface:
- Interface activity

- The chemical components can either add or detach from the solid at the interface between a crystalline solid and a fluid.
- There are three process that control the direction of this activity:
  - 1- Interface reaction
  - 2- Diffusion
  - 3- Convection

1- Interface reaction

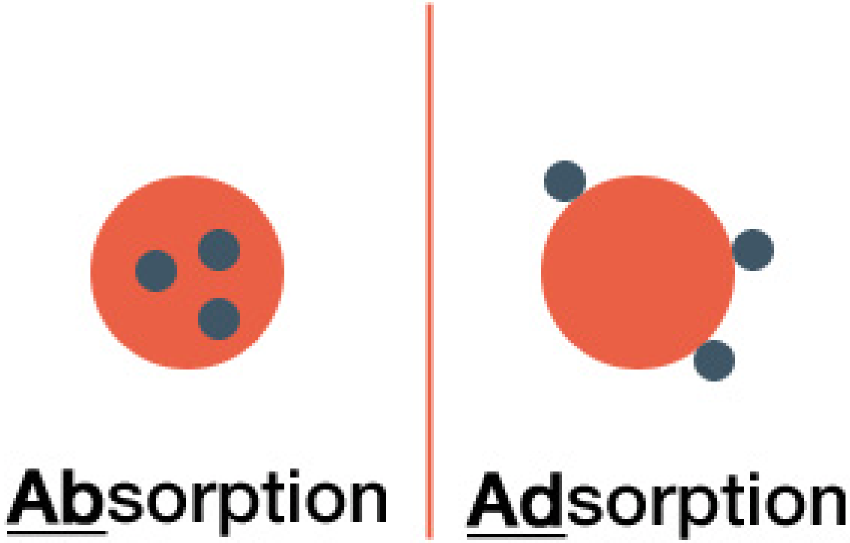
- For mineral to grow:

- For mineral to grow there must be Sorption (chemosorption) of growth components onto the surface of the crystal and incorporation into the crystalline structure as the process continues.

- Sorption includes: ***absorption*** *and* ***adsorption***.

- Absorption: is diffusion into the solid matrix.

- Adsorption: is diffusion onto the surface by complexation or surface polymerization (2 dimentasion) and also surface precipitation (3 dimension).



From: chemistrytwig.com

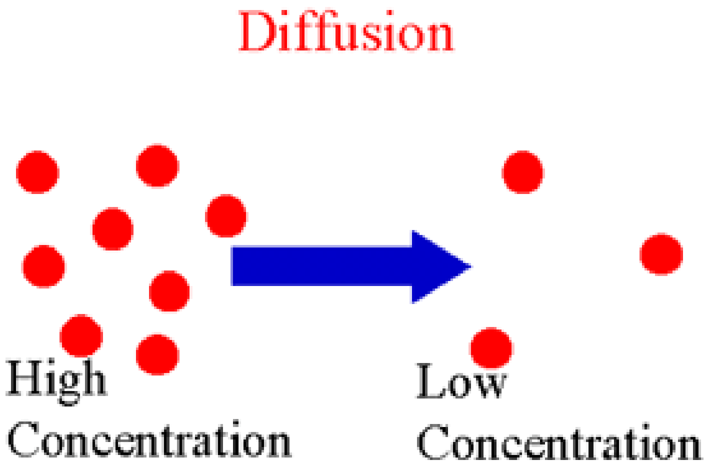
For mineral to dissolve:

- For mineral to dissolve there must be detachment (desorption) of chemical components.
- Desorption involves *detachment kinetics* and subsequent removal of these detached components from the interface region by either diffusion or convection.

- Note// the rate of dissolution is determined by the slowest of these processes.

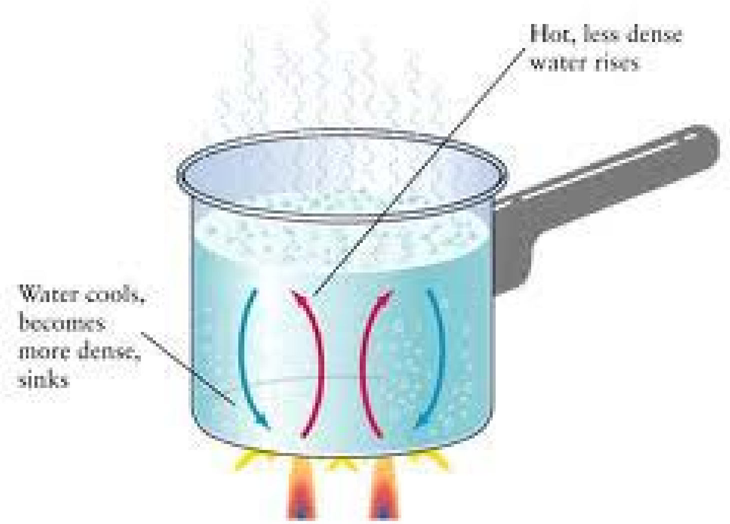
2-Diffusion

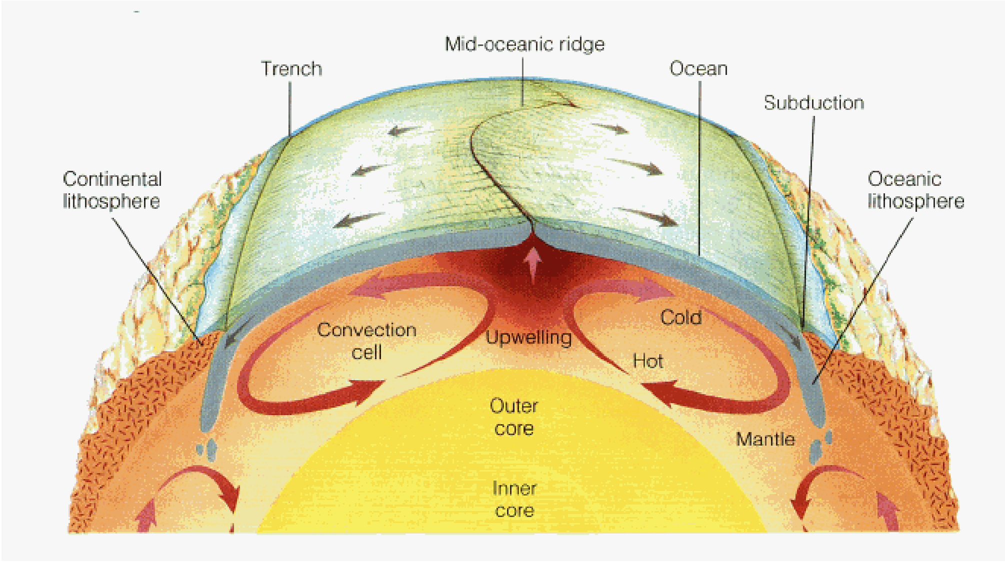
- A mechanism of supply of growth components.
- In diffusion, the solvent does not move. If the solvent is in motion (convection, advection), the growth components can be supplied to the interface without diffusion.
  - In reality, both diffusion and convection/ advection are likely to apply.
  - Note// the rate of growth is controlled by the slowest of these three processes.



From: www.occc.edu

Convection

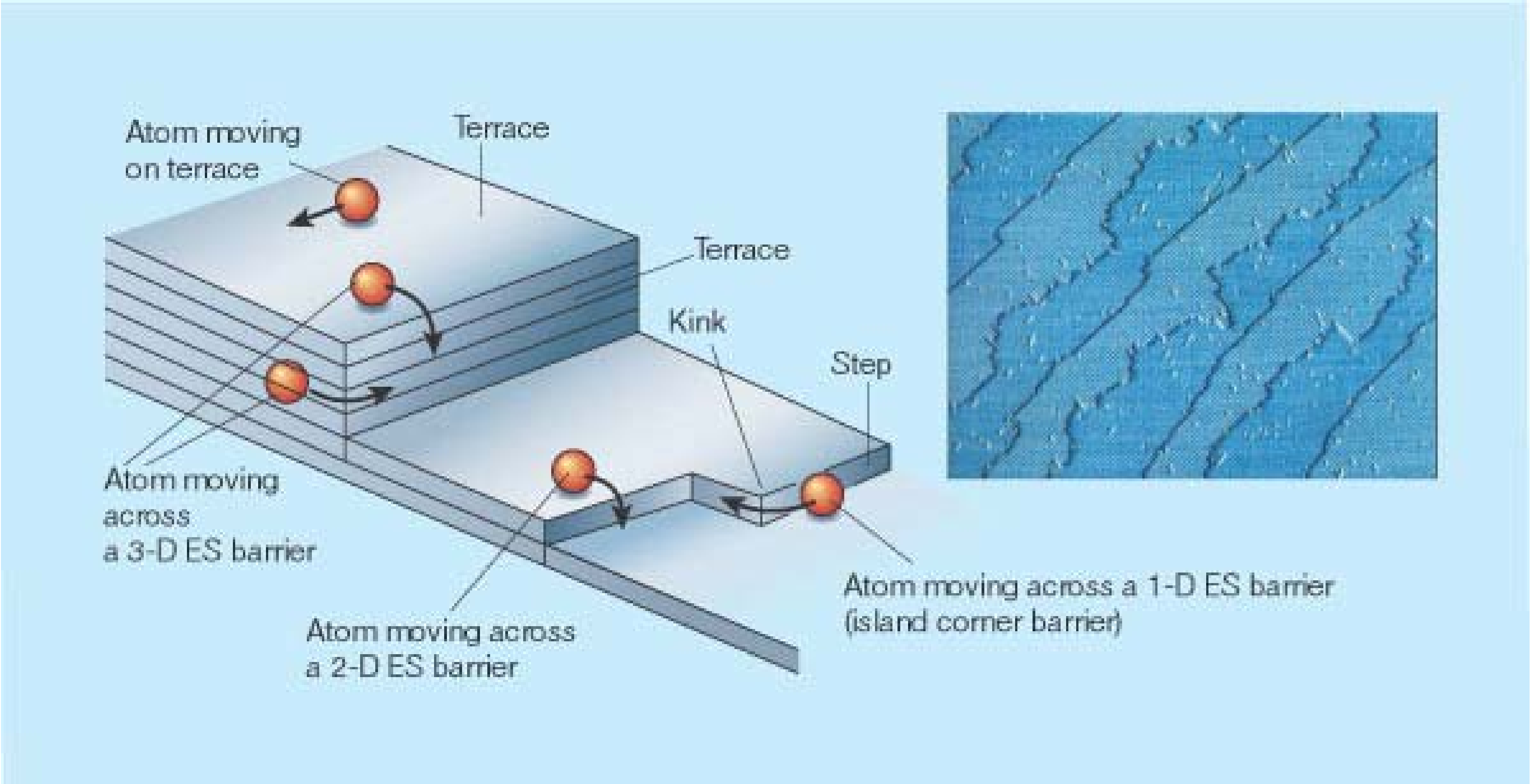

Hot, less dense water rises
Water cools, becomes more dense, sinks


Mid-oceanic ridge
Trench
Ocean
Subduction
Continental lithosphere
Oceanic lithosphere
Convection cell
Upwelling
Cold
Hot
Outer core
Inner core
Mantle

Crystal surfaces

- Crystal surfaces as sites of growth or dissolution are characterized by the physical topology of the surface and by the chemical bonding potential at various bonding sites on the surface.
- Chemical bonding at the surface is different from that within the bulk crystal, leading to different chemical properties at the surface.
- Any surface of mineral represents a discontinuity of the bulk crystal structue.

Crystal surfaces

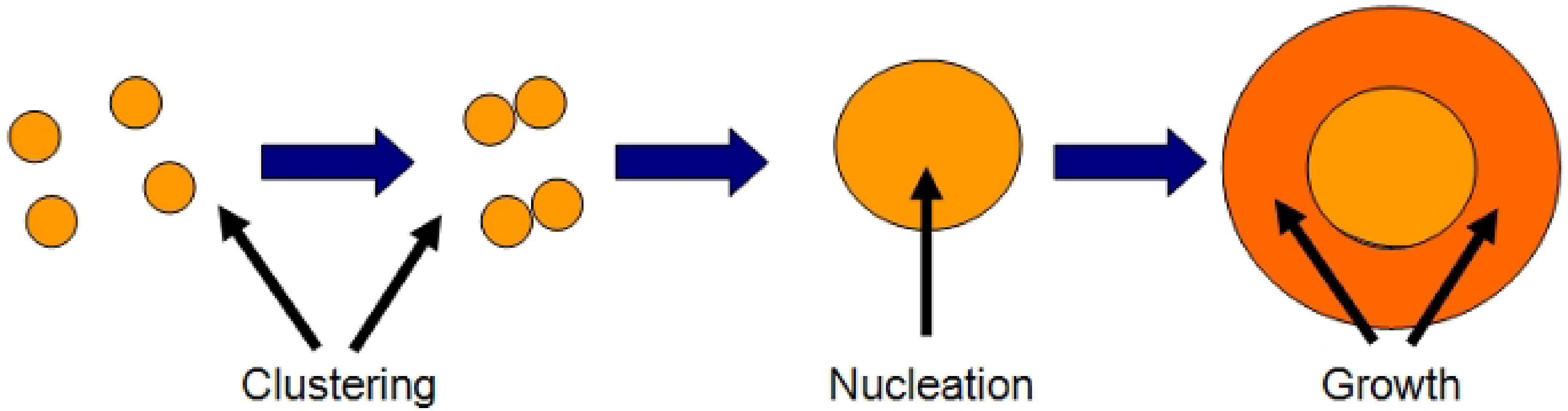


Growth sites on a crystal surface simulating layer spreading involving edge and kink adatom site along the advancing layer (Hibbard, 2002).
Photo from: www.nature.com

- Mineral surface may be rational (parallel to lattice planes) or vaccinal (not parallel to lattice planes); this has both attachment and detachment consequences.
- \- rough mineral surfaces are more reactive than smooth surface.
- \- because of variations in site density and bond strength, each of the surface microtopographic features is likely to dissolve or grow at different rates.

Nucleation in fluids

Nucleation is clustering of several unit cells (seed crystal) together to form nucleus.
Nucleus represents the template of crystal growth in which repetition of crystal structure can develop.



Crystal growth in fluids:

- Reasons for crystal growth:

- **1- lowering of the temperature** of the fluid that has the chemical potential to precipitate minerals.
- *Note//*
- *1- all liquids have a liquidus equilibrium temperature below which nucleation and crystallization can take place and above which the liquid phase state is maintained.*
- *2- cooling of liquid that capable to totally crystallization at specific liquidus temperature is rare in geological environments expect for the production of ice from water.*

- **2-Adiabitic undercooling:** effective undercooling happens as a consequences of changing the concentrations of solutions. (i.e supersaturation by evaporitation of water colvent).
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- Adiabitic undercooling can also be achieved by changing the composition of fluids. In this process there is exchange or redistribution of heat.

- Ex: mixing of salt water with meteoric groundwater along continental margins may lead to supersaturation and crystallization of calcite or quartz as the ionic strengths of solutions are changed.

- **3- Escape of volatiles from a liquid solution:** crystallization can also occur in response to escape of volatiles from a liquid solution, which is another example of composition change generation a effective undercooling.

- Ex: most silicate magmas contain dissolved H2O, which has the effect of depolymerizing silicate molecules. When this H2O separates out as a separation phase, as it does if the magmatic system intrudes to shallow (low pressure) regions or to the surface as a lava flow, linkage of silicate polymers is favored, being one step closer to the formation of stable nuclei and the crystalline structure of minerals such as quartz and feldspar.

Controls of crystallization

- There are four factors control crystallization:
  - 1- the attachment kinetics in the transfer of solutes to crystal structures at the crystal-liquid interface must be favorable.
  -
  - 2- there must be a viable mechanism, such as diffusion or convection, to supply growth components to the growth surfaces from the fluid environment.

Controls of crystallization

- 3- there must be a viable mechanism of removal of unwanted chemical components in the fluid at the interface, also by diffusion or convection.

- 4- there must be a means by which the heat of crystallization can be dissipated.

- *Note//1- if any one of these factors fails, crystallization is slowed or even arrested.*
- *2- the overall rate of crystallization cannot exceed the rate of the slowest step in the system affecting the growth rate.*

Mechanisms of crystal growth

- There are three mechanisms of crystal growth on crystal surface of minerals, these are:
- **1- Continuous growth:** attachments take place all over the surface more-or-less at the same time.
- **2- Layer spreading growth:** a single growth layer forms by attachments along a one-molecule (or one unit cell) thickness step before start of another layer.
- **3- Spiral growth:** growth occurs from screw dislocations by attachments along the sloping steps of continuous spiral.

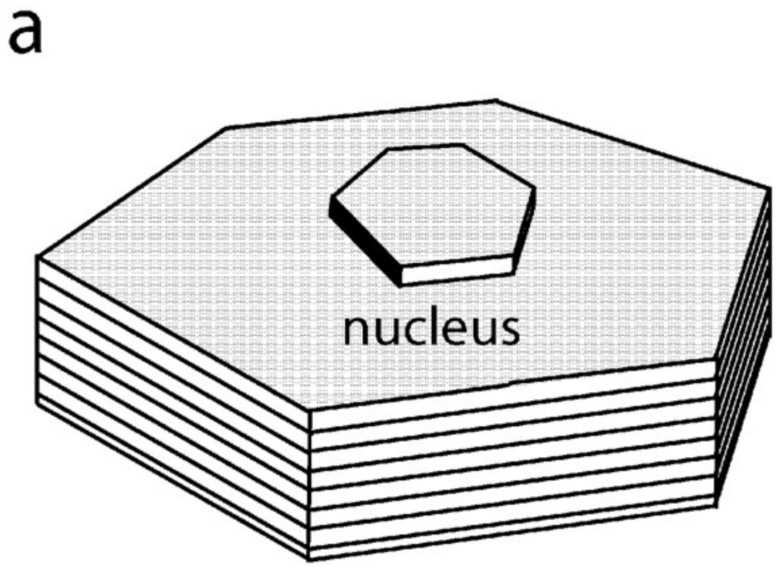

Photo from: claymin.geoscienceworld.org