TEXTBOOKS

RECOMMENDED REFERNCE BOKS:
2. Introduction to rock forming minerals: Deer, Howie and Zussman, ELBS, 1992 or latest
5. Fundamentals of Optical Spectroscopy and X-ray mineralogy: S. Mitra
6. Volumes of: Reviews in mineralogy: Mineralogical Society of America
WHAT IS A MINERAL?

A MINERAL IS A NATURALLY OCCURRING HOMOGENOUS SOLID WITH A DEFINITE CHEMICAL COMPOSITION AND A HIGHLY ORDERED ATOMIC ARRANGEMENT AND USUALLY FORMED BY INORGANIC PROCESS.
Knowledge of Mineralogy and Crystallography

Mineral definition indicates that mineralogy is related to:

1. Chemistry
2. Physics of the geological materials

Mineralogy is combination of three basic parts:

- **Chemical Mineralogy** - study of the chemical structure and properties of minerals
- **Physical Mineralogy** – Physical Properties of minerals
- **Crystallography** – the study of the internal and external morphology

The modern crystallographer is concerned with the chemical nature of the atoms within the crystals and Mineral Physicist is not content unless he or she is can relate the observed physical properties to both crystallographic and chemical properties

Mineralogy has become more advanced with advent of various Spectroscopic techniques:

- Environmental Mineralogy
- Industrial Mineralogy
- Geo-microbiology
- Surface Mineralogy
- High Pressure Mineralogy
- Crystal Growth
Why do present day earth scientist study mineralogy??

- Minerals are the **basic building blocks of all rocks**
  (Geology – science of earth : made up of rocks)
- **Have economic value**
- Important in modern **industry**, health and political activities
- **Geochemistry** of fluids – tied to equilibrium chemical reactions with minerals
- **Geophysics** – properties of rocks ultimately related to the physical properties of Minerals, etc.

More one knows about minerals – the better Earth Scientist one will – no matter what  
- F. C. Hawthorne

M.Sc – I 
GS - 423

**Micro to Megascopics mineralogy**

*What you learn in this semester ~ only 20 - 30% of the subject?*

*Understanding Fundamentals - KEY*
CRYSTAL GROWTH

1. How do well developed crystals form
2. How are chemical building blocks incorporated Into well ordered crystalline state
3. How accreting crystals go about for selection and rejections of ions from the nutrient

Need to understand basics of crystal growth:
(Important to understand Mineralogy and Petrology)

- Crystallization
- Nucleation
- Crystal Growth
- Crystal Habit
- Imperfections
CRYSTALLISATION: It’s the organization of atoms from a random state into an ordered symmetric arrangement.

Conditions: On account of changing - a) changing temperature, pressure and concentration

Growth of Crystals classified into:
1. Solid-solid Crystallization
2. Liquid-solid crystallization
   a) melt growth, b) solution growth and c) vapour growth

Solid–Solid crystallization; recrystallization
- initial and final – same crystal structure and chemistry,
- grains size increases through the movement of grain boundaries
  (Hunter, 1987, Ostwald ripening- textural maturity)

Definition of Ostwald ripening
Many small crystals form in a system initially but slowly disappear except for a few that grow larger, at the expense of the small crystals. The smaller crystals act as "nutrients" for the bigger crystals. As the larger crystals grow, the area around them is depleted of smaller crystals

120° Angles – Triple Grained Intersections
- seen on similarly sized grains
- usually common in monomineralic metamorphic rocks (?)
- Static stress regime
Geological Process: Marble, Quartzite – solid-solid crystallisation

Liquid-Solid Crystallisation: e.g. for solution crystallisation – NaCl dissolved in water..

Water evaporates → solutions contains more and more of Na\(^+\) and Cl\(^-\) ions per unit volume

If evaporation of water – slower- ions of Na and Cl with group themselves together – one or few crystals
If evaporation is water – faster- many centres of crystallisation – many small crystals

Crystal from solutions:

a). temperature, b) pressure and c) evaporation of solvent

A crystal formation from melt is same way as solution, but crystallisation from vapour is less common than from solution and melt (snow flakes from air laden with water vapour)

First stage of growth: NUCLEATION

Nuclei is the result of the coming together of various ions (solution or melt) to form the initial regular structural pattern of the crystalline solid

Any change favoring transfer of energy – kinetic motion to interatomic bonds promote greater aggregation of atoms……

• decrease in temperature
• Increase in pressure
• Increase in concentration

Growth commences only after the seed or nuclei has been formed and becomes sites for further crystal growth
Nuclei is the initial product of ppt or crystallisation (*critical step of growth*)

-It is the result of coming together of various ions (sol or melt) to form the Initial regular structural pattern of the crystalline solid

Nucleation Problems:
- Tiny crystal have high ratio of surface to volume
- Surface ions are unbalanced….
  - High surface energy of initial crystal – low stability- dissolution

Nucleation does not occur at the anticipate conditions:
- e.g. at atm pressure, water freezes at 0°C—but not true – water is cooled below 0°C (**supercooled**)

Clean water = -5°C; Ultra pure water = -15°C (**why**) – presence of impurities

Two types of Nucleation:
- a) heterogeneous – presence of discontinuities in the system
- b) homogenous – not dependent on presence of foreign bodies

Is there any energy barriers for homogenous nucleation's ??
- thermal energy that keeps the two particles separate or coming together (i.e. energy required to form a new surface)

Atoms and molecules come together form chemical bonds – gives back some energy to the system
- On further addition system energetic changes – there is critical pt – process becomes spontaneous + irreversible
**Nuclei**: Understand the term meaning “most stable” or lease energy state

What keeps the molecules together?? Or why molecules need to come together to form seed nuclei?
-Continuously wandering and vibrating – why not disperse get further apart – GAS
(opposite charge or force of attraction > repulsion (less thermal energy)

**Liquids always retain the shape and adapt to the vessel it pored**

-e.g. Evaporating salt lake: conditions appropriate for the ppt of NaCl:

-Na\(^+\) and Cl\(^-\) are combining together in a cubic array of alternating ions of Na and Cl as required by the structure of NaCl

– they have to find the most stable conditions or arrangement. How do they do this?

They plane themselves in a manner that every +ve Na is surrounded by –ve Cl and every –ve Cl is surrounded by -ve Na

**Resulting in a chessboard arrangement in 3-dimension**
Nucleation:
- Driving force (supersaturated or supercooled)
- Critical radius needed to survive nucleation
- Dangling bonds per unit area on the surfaces decreases as size of nuclei increases

Heat and Mass transfer

Solution – Mass transfer > Heat transfer
Atoms and ions – transported far away.
On crystal surface – are incorporated
Mass transfer – driving force [growth temp low]

Melt – Heat transfer > Mass transfer
Crystal growth rearrangement of atoms at the solid-liquid interface. Heat transfer is the driving force required for atoms rearrangement to occur [growth temp high]
Formation of a crystal either from a melt or from solution or in a solid medium (metamorphic mineral growth) involves three processes:

1. Nucleation
2. Subsequent crystal Growth
3. Diffusion of chemical species

Relative rates of each may vary and therefore have considerable influence on the final texture of the resulting rock.

Diffusion rate of a chemical species is faster at higher temperatures and material of low viscosity. It is slow in highly polymerized viscous melt (silica rich).

Diffusion > in fluid > glass > crystalline solid

Pegmatite's – have large crystals
Residual fluid phase (H₂O acts as flux)
Large amounts of supercooling??

a) critical nuclei diminishes
b) high rate of nucleation
   
   • elements mobility greatly reduces – increased viscosities
   • atoms do not have time to rearrange to crystalline state before complete solidification

GLASS

Low degree of super cooling – few nuclei per unit time – further growth of crystals

IGNEOUS ROCKS: coarse grained – forms at depth – ambient temp is high – low degree supercooling

Result?? Fewer nucleation centres → larger crystals

VOLCANIC ROCKS: fine grained – at the surface
rapid cooling

Highly supercooled – high rates of nucleation centres -
Low crystal-growth rates → fine grained (OBSIDIAN)

Nuclei serve as templates for further accretions – which
further leads smooth crystal surfaces by successive addition
of atomic layers or departure ------unidirectional spikes
Accretion unit seeks attachment site of maximum coordination on the surface of a nucleus – results in reduction in the free energy of the system – transfer to the Crystal phase.

How??

Consider coordination position -1- higher than 2- so the free energy drop will be greater here and Therefore accretion site...is favored than a step

Result in atoms joining in crystalline solid will be Preferentially added in extension of developing Layers – leading to the formation of planar faces Such as (100), (010) and (001)

The initiation of a secondary layer may take place by secondary nucleation of new growth unit upon a completed face.

Such units seek positions away from an edge Where greatest free-energy drop is provided
Coordination of different kinds of possible attachments sites for ions on an existing crystal

Maximum four coordination interior ions and Accreting ions can attain cordinations of
-three at reentrant positions (chaistolite)
-two on faces and
-one on corners

Reduction of energy by transfer to the system

-Greatest reduction of free energy occur at sites Of higher coordination are occupied

The total energy associated with each attaching of Ions is shown of left figure.

Shaded portion – loss of energy for various attachments

Filling at reentrant site lead to planar faces

Growth rate is reciprocal to translation and hence slow growing face becomes increasing prominent and the final shape tends to be reciprocal to the shape of the structural cell
Growth steps:
Growth may occur against discontinuities called – Dislocations or edge dislocations

The discontinuity is across a plane, spiral dislocations – discontinuity has the form of screw axes

Both are result of misplacement of atoms in consequence of included impurities, Mechanical stress or growth discontinuities.

e.g. differential compression – dislocation along glide planes

Several differently oriented discontinuities may be present simultaneously present in a structure and then each may provide a Step against which growth units find Maximum coordination
**Dendritic Crystallization:**

Special Mechanism for rapid crystal growth is more common than generally thought-

The term comes from the root-like habit of crystals such as snowflakes or dendrites of manganese hydrous oxides - Mistaken for plant fossils

1. Nucleation and development of favored accretion direction
2. Rapid growth of rod-like protrusion, coupled with the crystallographically controlled oriented side branches
3. Backfilling of interstices
Crystal Imperfections

[Diagram showing crystal imperfections with various structures and patterns.]

- Slower
- Faster

[Graph showing radius ratio vs. cell edge with different crystal structures indicated.]
Crystal Habbits

**Fig. 5.12** Morphology of snow crystals as a function of supersaturation and temperature. The line W gives the saturation vapor pressure with respect to supercooled water (after Nakaya, 1954).
SURFACE TOPOGRAPHY STUDIES

Screw dislocation

SEM Image
Sectoral and Intrasectoral zoning of REE – Role of Surface structure

Trace element charge and size, electronegativity, crystal field effects, and crystal growth rate, as well as state variables such as temperature, pressure, and composition, have all been identified and studied as factors affecting trace element partitioning.

Recently - several authors demonstrated - the role of surface structure on the partitioning of elements into crystal

Differential incorporation of trace elements onto different crystal surfaces during growth, leading to sectoral zoning/intrasectoral zoning - controlled by surface structure.

Intrasectoral zoning describes compositional differences between time-equivalent portions of a given sector of a single crystal.

Apatite, Ca5(PO4)3(F,OH,Cl), is a ubiquitous accessory mineral in igneous rocks and its presence can strongly influence the trace element evolution of magmas.

Several different types of compositional zoning are found in minerals, each of which provides unique information about the formation and growth history of a crystal.

Most familiar type of compositional zoning - concentric zoning, in which the contact between two portions of a crystal with different compositions is parallel to the growth surface.

Concentric zoning most commonly reflects changes in the environment of growth over time (changes in chemistry, temperature, supersaturation, etc.).
important substituent cations include

For $\text{Ca}^{2+}$ we can substitute $\text{Na}^+$, $\text{Sr}^{2+}$, $\text{Ba}^{2+}$, $\text{Mg}^{2+}$, $\text{Eu}^{2+}$, $\text{Pb}^{2+}$, $\text{Mn}^{2+}$, $\text{Fe}^{2+}$, $\text{Fe}^{3+}$, $\text{Eu}^{3+}$, $\text{Y}^{3+}$, $\text{LREE}^{3+}$ and others.
For $\text{P}^{5+}$ (or $\text{PO}_4^{3-}$ group) we can substitute $\text{Si}^{4+}$, $\text{SO}_4^{2-}$, $\text{CO}_3^{2-}$, and others
A common substitution for REEs is: $\text{REE}^{3+} + \text{SiO}_4^{4-} = \text{Ca}^{2+} + \text{PO}_4^{3-}$
Growth occurs on the entire surface of a crystal (i.e., on all crystal faces), any given concentric zone is comprised of time-synchronous portions of all the sectors [regions of a single crystal that have grown by incorporation of growth units onto a given crystal face) contained therein.

Hence - upon termination of growth the last concentric zone to form is bounded by the crystal surface itself, and the different regions of that surface-most layer are coeval or time-synchronous.

A second type of zoning found in minerals yields information about growth mechanism and the subtleties of element incorporation during growth.

Two variations of this type can be identified - sectoral and intrasectoral zoning.

Figure 1. a) Schematic diagram of a hexagonal crystal with one of the {1010} prism sectors outlined in bold dashed lines. b) A three-sided growth hillock has been drawn on the prism face and one of the subsectors is shaded.
Sectoral zoning is represented by compositional differences between time-equivalent portions of different sectors. Compositional interfaces for sectoral zoning correlate with growth sector boundaries, which, if present, cut across concentric zoning.

Such compositional differences can only arise during growth of a crystal, and correlation of compositional differences with different crystal faces suggests that the characteristics of the crystal surface lead to its formation.

A compositional difference between time-equivalent portions of different subsectors is known as intrasectoral zoning.

Growth on a crystal face occurs by the spiral mechanism, hillocks will generally develop on that face.

e.g. Of spiral growth
Qualitative and quantitative compositional analyses of regions within individual sectors and subsectors were conducted using cathodoluminescence (CL) microscopy, electron probe microanalysis (EPMA), and synchrotron X-ray fluorescence microanalysis (SXRFMA).
Apatite samples show optical anomalies that correspond directly to time equivalent portions of different sectors and subsectors within single crystals. Sectors under \(\{0001\}\) are uniaxial negative, whereas sectors under \(\{1011\}\), \(\{1121\}\), and \(\{1010\}\) are biaxial. Subsectors associated with different vicinal faces within these individual sectors range in 2V from 2° to 15°.

**Surface structure not only plays an important role in differential partitioning of trace elements into apatite during growth but also influences ordering of atoms, leading to dissymmetrization.**
Understanding the petrogenesis of hydrothermal deposits is very important, as they are a major source of ore minerals. Trace elements, especially the rare earth elements (REE), often substitute into certain hydrothermal minerals and can provide important information about the genesis of the deposit.

Fluorite is a common gangue mineral in hydrothermal ore deposits. The REE substitute readily into the $\text{Ca}^{2+}$ site in the fluorite structure, making fluorite an important mineral for REE studies of hydrothermal deposits.

To fully deduce the petrogenesis of any geologic deposit, whether crystallized from a magma or precipitated from a hydrothermal solution, it is first essential to understand the specific thermodynamic, kinetic, and mechanistic factors that govern crystal growth processes and trace element incorporation.

Often trace elements are sectorally zoned in minerals. A growth sector is a volume of a crystal that grew by incorporation on a specific crystal face. Sectoral zoning is defined as compositional differences between coeval portions of symmetrically nonequivalent growth sectors.

Two theories - To explain – sectoral zoning.
1) Differential growth rates among symmetrically nonequivalent crystal faces have been documented as a controlling factor in the partitioning of trace elements in minerals.

2) Role of a mineral’s surface structure has recently been recognized as a primary factor governing differential partitioning and trace element chemistry in such minerals as apatite, calcite and topaz.
Mechanisms controlling element incorporation at the mineral–water interface are unique to a given mineral system or are more fundamental in nature.

REE are a useful tool for studying differential incorporation – Chemically - behave similarly and - there is a systematic decrease in ionic radius with increasing atomic number makes them an excellent tool to probe the affects of the size of sites of incorporation.