L9: Crystal growth and nucleation

Thursday, August 27, 2020   14:03

Time on task: 2 hours (material posted on Oct 5th, Student hours: Monday Oct 19th and Wednesday Oct 21st)

Goals:
Upon completion of this lecture, you should be able to:
1. Explain the concept of nucleation and nucleation energy
2. Understand the theory of crystal growth and its limitations.

1. Crystal growth Environments

The environments in which a crystal can growth are very diverse: under vacuum, at the surface (1 bar – room temperature), in depth (high pressure and high temperature), in water, in air…

However, for each mineral, you need very particular conditions to growth. And this is particularly true in case of minerals that contain relatively rare elements, such as zircons, ores. The first condition for a mineral to growth is that the constituent elements (or ingredients) are <u>available</u>.
E.g.: The formation of quartz requires Si and O, the formation of pyrite (FeS_2) requires Fe and S.

Hence, the mineralogy of any rock is limited by the bulk chemical composition of the rock.

In nature, it exists three main environments for mineral growing:

1) In vapor phase
e.g., solar nebula, volcanic fumaroles

Sulfur crystallization in volcanic fumaroles on Vulcano, Italy

2) In solution: aqueous or magmatic

e.g., precipitation of NaCl in the great Salt Lakes
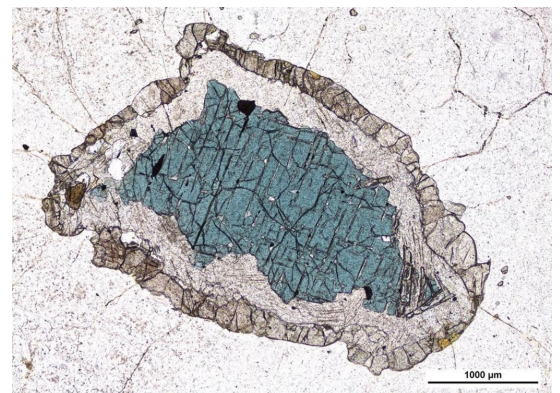   Crystallization of olivine in magmas

3) In solid: metamorphic reactions
solid-state phase transformation: mainly in metamorphic rocks.
This will occur when the fluid/rock ratio is very low
=> extremely slow diffusion.

Sapphirine breaking down into orthopyxoxene and sillimanite
PPL thin section picture - *Credits: Chris Clark*

2. Nucleation

Three possible conditions for a mineral:
- Stable
- Metastable
- Unstable

Most phase transformation (except a polymorphic displacive transformation) requires energy to occur, called activation energy.

Definition: **Activation energy** = energy required to transform a metastable mineral to a stable mineral.
The presence of a metastable mineral will depends on:
a. How big this activation energy is
b. For how long the metastable mineral stays outside of its field of stability
c. How far the considered pressure and temperature conditions are from the field of stability of the metastable mineral.
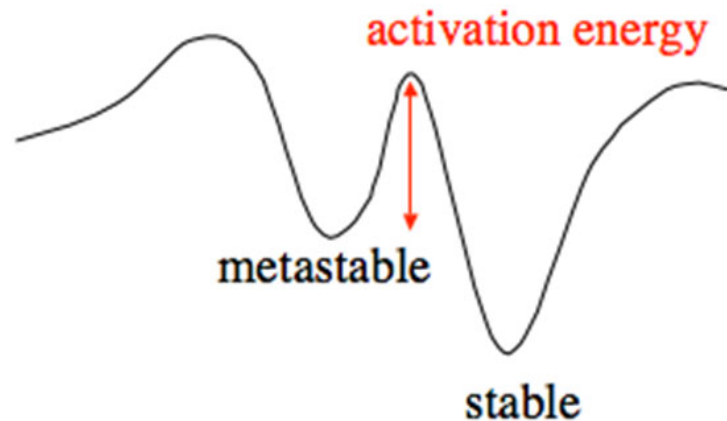
Nucleation and crystal growth follow the same logic.

The two conditions for crystal growth to happen are:
(1) being in the field of stability of the crystal (i.e., being in the appropriate pressure and temperature conditions)
(2) having the constituent elements available.

In order to growth a mineral from a fluid - in this case, the fluid can be a magma, water or even air; in other word, some sort of reservoirs where the ingredients are available that can be added to the crystal - you need two processes to occur:

<p align="center"><strong style="color:red">Transport and Nucleation</p>

Transport is the transport of the ingredients into the fluids to the surface of the crystal that is growing. In other words, if you don't have the ability for the chemicals to come in contact with the nucleus, it's not going to growth any bigger.
Transport of an element is defined by its **diffusion coefficient** (ie., how fast the element can diffuse through a substance, fluid or solid) and **kinetics of the reaction** (=reaction rates).
Different elements can diffuse (i.e., be transported) at different rates, which can cause some minerals to become stable while others remain metastable.
Kinetics depends on pressure, temperature and composition of the system. Reactions tend to happen more quickly at higher temperatures.

Nucleation is the initial precipitation of a mineral, the initial growth.
Definition : **Nucleation** is the initiation of crystal growth – you can call them embryos, seeds or nucleus - in a fluid.

Nature always try to minimize its energy. Hence, in order for nucleation to occur, the crystallization of a mineral must result in reducing the energy the fluid on its own. This will be the case if you are in the field of stability of the mineral. However, this is not enough. You need to pass through the **nucleation energy barrier** (i.e, the equivalent of the activation energy for crystallization)

We can use the change of Gibbs free energy of formation, known as ΔG_f, to talk about the energy of nucleation.

Determining the Gibbs free energy of <u>formation for a crystal</u> needs to consider both the volume and surface of the precipitating crystal:

Consider a crystal of volume V and surface S:

1) Volume energy.

$$G_V = [G_f(crystal)-G_f(fluid)]*V$$

If we are in the field of stability of the crystal, $G_V < 0$ and the mineral can *potentially* precipitate (corresponds to condition #1).

2) Surface energy = interfacial energy

$$G_S = \gamma S > 0,$$

where γ is the surface energy per unit area.
G_S is always positive: it consumes energy to produce crystal surface.

The Gibbs free energy of formation is:

$$G_f = G_V + G_S$$

A crystal will grow only precipitate if **$\Delta G_f < 0$.**
The energy required for the nucleation and grow of the crystal increases with the surface/volume ratio.

L9: Nucleation - practical aspects

Monday, August 31, 2020   19:11

Let's consider the example of a perfect spherical crystal, of radius r, in its field of stability (i.e., $\Delta G_V < 0$)
- Volume of a sphere: $(4\pi/3)*r^3$
- Surface of a sphere: $\pi*r^2$

$\Rightarrow G_f = G_V*(4\pi/3)*r^3 + G_s*\pi r^2$

G_V is proportional to $-r^3$ and G_S is proportional to r^2. Hence, for small values of r, the $G_S > -G_V$ and ΔG_f (i.e., the slope of G) > 0. The mineral won't precipitate because it would consume energy to make it grow.

For higher value of r, $G_S < -G_V$ and $\Delta G_f < 0$. The mineral will grow as increasing its radius will reduce the total energy of the system.

The most important diagram of this lecture →
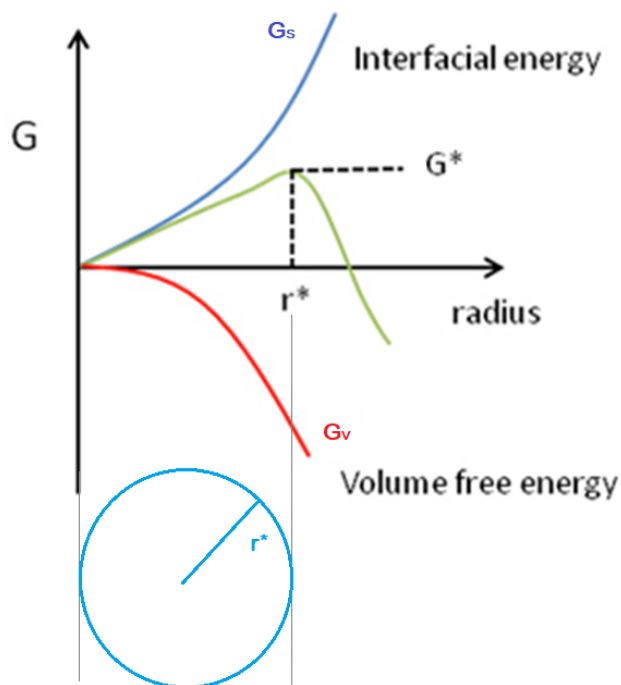
r* is the **critical radius**: initial nucleation always requires a certain amount of energy for the crystal to start growing. Starting at this point, the level of energy drops and the reaction is <u>self-continuing</u>. But you need to have sufficient energy to reach this point. So what this diagram is saying is that nucleation sometime is one of the hardest things to get started.

The required energy to start the nucleation is called **nucleation energy (G*)**. This also tell us that the crystal has to have a minimal size to be stable (and to grow).

Some minerals have a very low nucleation energy . For instance if you place salt in water, mix enough to dissolve the salt, and then put a string in the water, salt is going to crystallize instantaneously along the string. Halite has a very low nucleation energy.

Some other minerals don't nucleate even if they should. The best example is dolomite. We don't really understand what's going on with dolomite. Dolomite is such a stable mineral, it has such a low solubility, that technically, it should form in the oceans instantaneously and it's not the case. So something is blocking the reaction: perhaps the nucleation energy, the transport process. It's called the "dolomite problem".'
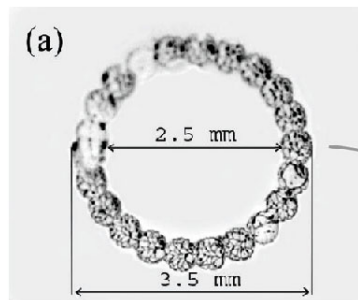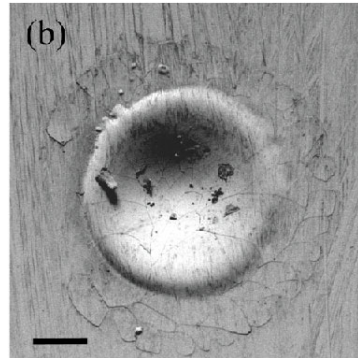
2.1.Homogeneous vs. heterogeneous nucleation

In order for some crystals to form, you must overcome the nucleation energy barrier, or ultimately add more nuclei.
In fact, we distinguish between **homogeneous** and **heterogeneous** nucleation.
During homogeneous nucleation, the nucleus has to form from a pure fluid reservoir.
During heterogeneous nucleation, the nucleus forms on a preexisting surface (e.g., dust, other nuclei).
Because creating surface always consume energy, heterogeneous nucleation requires less energy than homogeneous nucleation.

Fun fact: Champagne flute manufacturers engrave small marks on the glass (usually with a laser) to promote heterogeneous nucleation of bubbles creating charming bubble trains in motion in the champagne bulk.
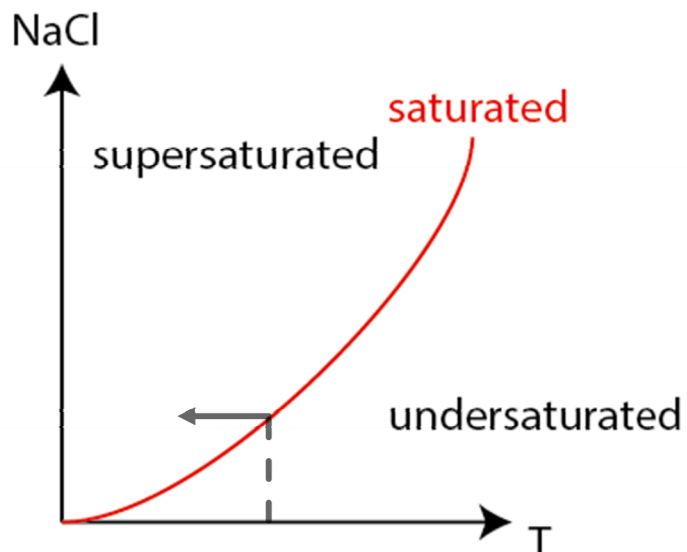

Credits: Liger-Belair et al., 2009, Journal of agricultural and food chemistry

2.2 Supercooling

The last concept that I want to introduce on nucleation is Supercooling. This notion is particularly important for the homogenous nucleation for which the energy of nucleation can be significant.

In our first example, we will consider the system halite + water.

At a given temperature, when you mix salt and water, if you can dissolve all the salt, it's because you are undersaturated; you still have some crystal of salt and you are supersaturated; or you can be in a perfect equilibrium and you are saturated.

So now, let's come back to our concept of nucleation energy and supercooling. In theory, if you are on the saturation curve and you decrease the temperature by a fraction of degree, you become supersaturated and you should start to precipitate halite. However, because you need a certain amount of energy (G*) to nucleate halite, you might not start to crystallize right away.

Eventually, if you wait enough time, salt will crystallize. That's correspond to the point b discussed at the beginning of this lecture: time is one of the factors controlling the metastability of the system. If the system is supersaturated but crystallization did not start yet, the system is metastable.

Alternatively, you could decrease the temperature a little bit more to accumulate the energy bigger than the nucleation energy. That would correspond to the point c = how far from the saturation curve I am.

Finally, for a magma, we don't use the term supersaturation, we use the term **supercooling** but the principle stay the same. If a phase diagram predicts that you should start to crystallize at a certain temperature (base on thermodynamics), in practice, the magma is likely going to start to crystallize at a lower temperature. Note that this work both ways, if you progressively increase the temperature to melt all the crystals, your observed liquidus (i.e., the magma is completely liquid, there is no crystal) is likely going to be higher than the liquidus temperature predicted by thermodynamics (and faster is the increase of temperature, bigger will be the difference). This is way we often do <u>direct and reverse</u> experiments, to better bracket the true liquidus temperature.

L9: Crystal growth

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3. Crystal growth

Once you have your nuclei formed, you still have to worry about your surface energy: you want to try to minimize the amount of energy that you want to spend in creating new surfaces.

It exist three types of faces on which a crystal can grow:

- F for flat
- S for stepped
- K for kinked

Energy requested to grow on faces: F > S > K

In fact, assuming that the next growing step is the addition of a small cube (as represented here), a face F will requires the formation of 5 additional faces, the face S, will require 4 additional faces and the face K would require 3 additional faces for the same volume.
In other words, the surface/volume ratio is the highest for F faces and the lowest for K faces.
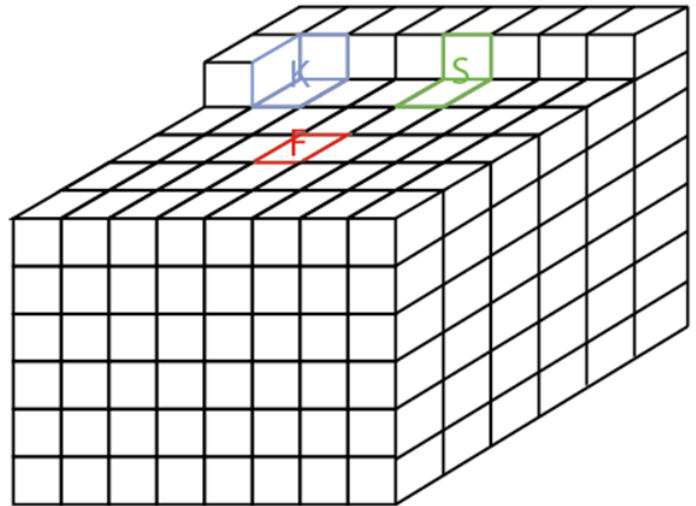
Hence, the kinetic of growing are not going to be the same between each faces. A face F will grow more slowly than a face S or K.

The (counter-intuitive) consequence is t**he faces with the slower kinetics are the most developed**.

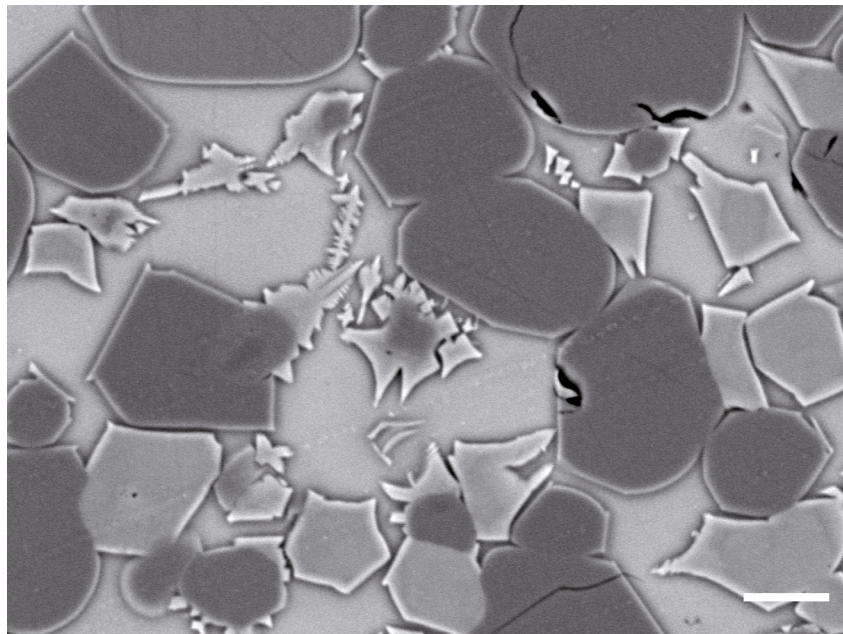In general, crystals grow faster along longer dimensions of the unit cell.
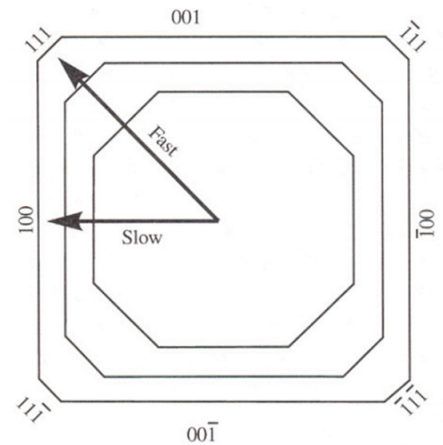
4. Dendritic crystals

If nature always try to minimize the surface/volume ratio, what's going on with the dendritic crystals???

Dendritic iron-manganese oxide in limestone -
you can see some great examples of these on the wall of the Marriott Library on campus

Backscatter scanning electron (BSE) image of a partial melting experiment of a peridotite at 1 GPa and 1290 °C. Olivine are dark and roundish, orthopyroxene are dark but more angular, can present some dendrites, clinopyroxene are the light angular crystals and the light material with low relief is glass (i.e., quenched magma).

Dendritic crystals have an extremely high surface/volume ratio. Hence, they required a lot of energy to be produced and are not considered as a stable form of the crystal.

The process that controls the dendritic crystal growth is the **transport**. In fact, dendritic crystal occur when the **growth rate is limited by the rate of diffusion** of solute atoms to the interface.

This mainly occur during a rapid cooling. In fact, cooling tends to increase the viscosity of the fluid and to slow down the diffusion. Some crystals form dendrites more easily than others.

The BSE image shows an example of an experimental sample cooled at 50°C/s. We can see that while the olivine (dark) tend to have euhedral habit, pyroxenes (light) developed dendritic rims.

Note that dendritic growth has recently be revealed as more common than we thought. In facts, phosphorous maps performed on some crystals, such as olivine, that often present euhedral shapes (with a low surface/volume ratio), reveal the existence of a skeleton suggesting that crystal growth was first dendritic and that the euhedral shape was acquired later, during additional growth or **ripening** of the crystal.


3-D Solution
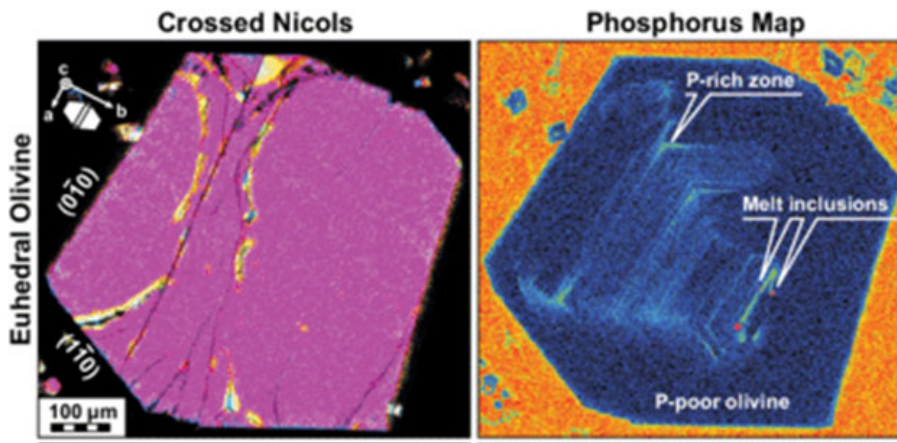
Credits: Welsch et al., 2014, Geology
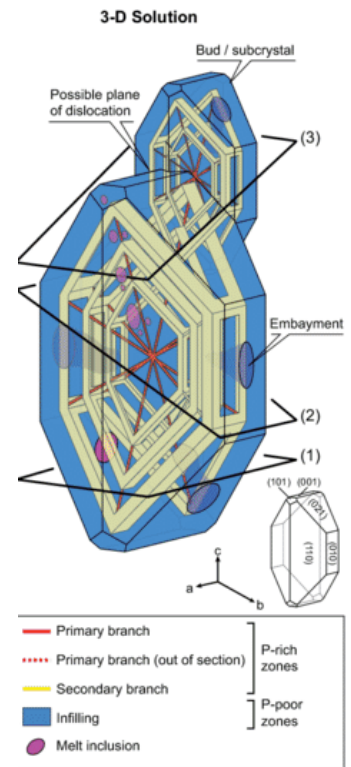
Definition: Ostwald ripening is a thermodynamically-driven spontaneous process that occurs because larger particles are more energetically favored than smaller particles: unlike crystal growth that occurs while the temperature is decreasing, Ostwald ripening occurs at a given temperature and consists into preserving the same total volume of crystals in the system but decreasing the total surface by dissolving the small crystals to develop a smaller number of larger crystals.
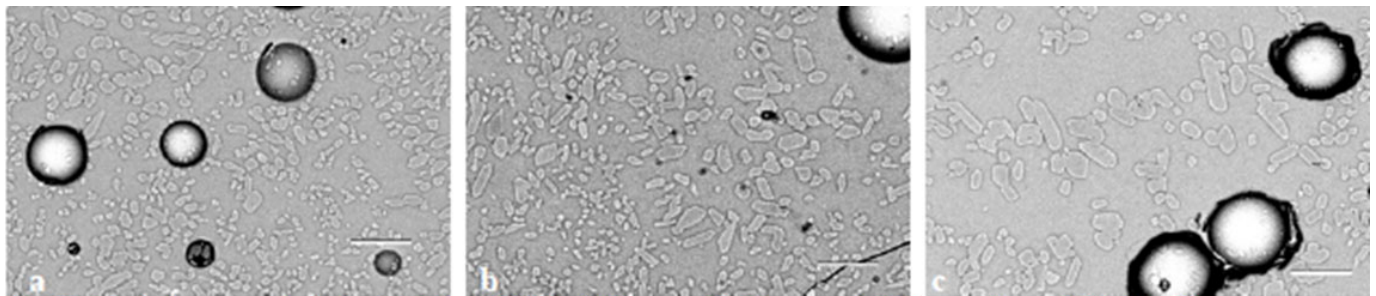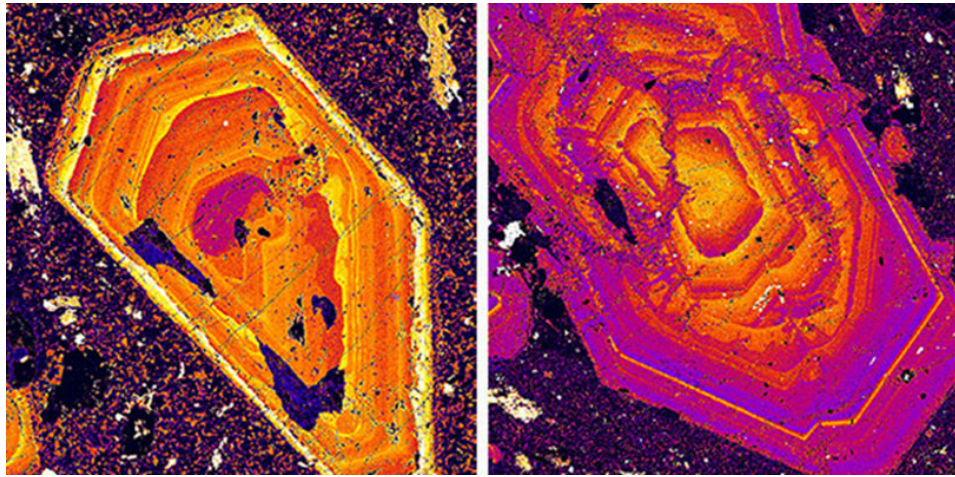

Experiments on diopside at 1300°C after 2, 6 and 24 hours.

$y = 0,2192x - 0,3347$
$R^2 = 0,814$
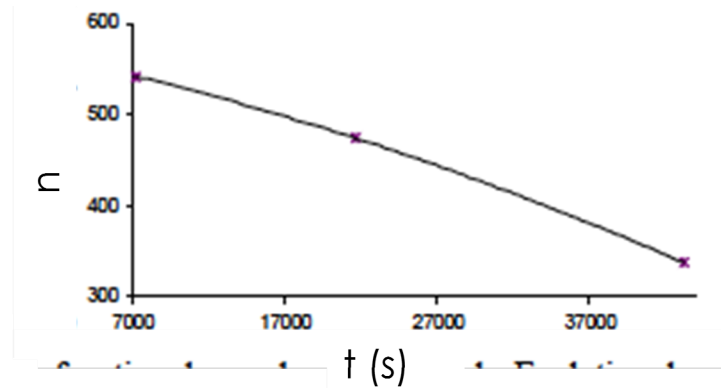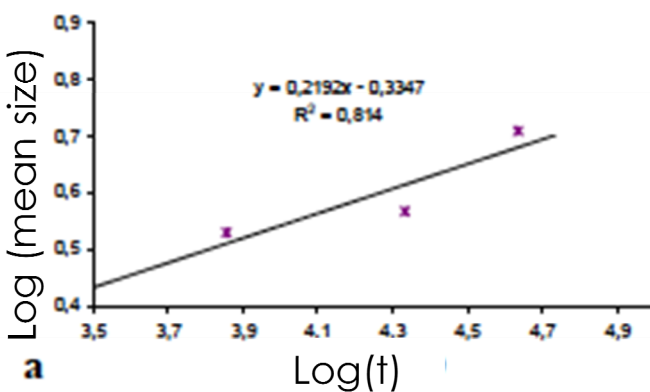
The average size of the crystals increases and the number of the crystals (n) decreases with time

5. Zoned crystals

Element maps showing Ca and Na zonation in plagioclase.
Source: http://serc.carleton.edu/details/images/8598.html

Zoned crystals are due to the change of the composition of the mineral during their growth. The presence of zoning can reveal important information on the environment of the crystal during its growth. For instance, plagioclase often exhibit complex zoning such as displayed in this photograph, interpreted as series of new magma reinjection in the magma chamber.

Note that plagioclase zonation is often visible in thin section - XPL (you don't need to do element maps at the electron probe to observe this).

Thin section - XPL - FOV = 4.5 mm
Zoned plagioclase in diabase - R192 - G&G teaching collection
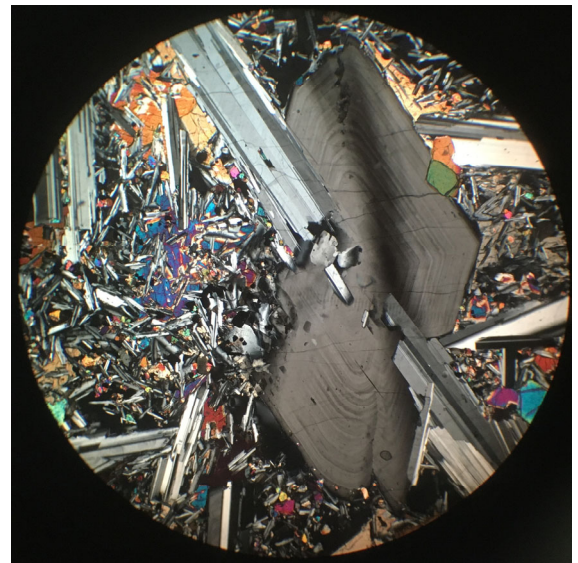
L9: Personal assessment

Tuesday, September 1, 2020   10:36 AM

After reviewing this material, you should be able to answer these questions:

****Multiple choices possible!****

1) **What are the two processes that control crystal growth?**

2) **What is the crystal defect that promotes crystal growth and why?**

3) **Ostwald ripening is a thermodynamic process**

A – that results in increasing the total crystal volume of the magmatic system
B – that results in decreasing the total crustal surface of the magmatic system
C – happening during the crystallization of the magma
D – happening at constant temperature

4) **Dendritic crystals**

A – are crystal with prismatic unit cell
B – are metastable
C – can form during slow cooling
D – can be caused by supercooling

5) **Crystal growth: Look at this crystal, in which direction it is more likely to growth and <u>why</u>?**
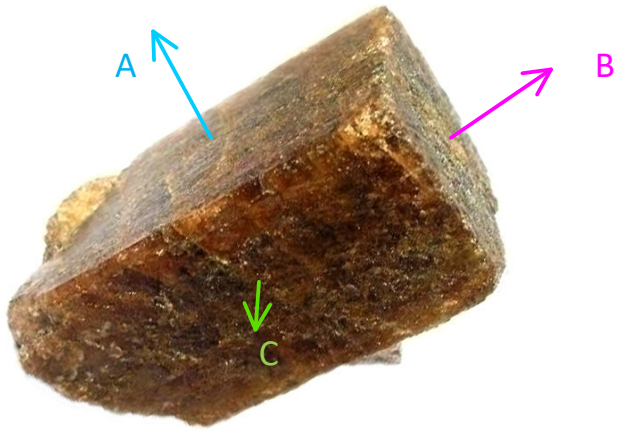
6) Augite crystals can, sometimes, display zoning because:

A – augite is a solid-solution
B – augite is a mineral found in volcanic rock
C – augite contains calcium
D – augite is a clinopyroxene