

## Lecture notes for GEOL3020

**Mineral Thermodynamics** - This is a prelude to mineral associations. In your studies of systematic mineralogy you have been noting the occurrence of minerals.

**Rock** - defined as an aggregate of one or more mineral. The study of rocks is known as petrology. Petrology includes the identification of minerals and their associated textures (size and shapes) and abundance.

The information derived from petrology is used to understand the origin and formation of the rock. So, not only does a geologist need to be a mineralogist (for identification purposes), but she/he must also be a physical chemist and biogeochemist to know something about conditions under which near-surface minerals undergo reaction or change.

Minerals form and disappear in response to changes in specific physical and chemical conditions. The role of the geochemist is to determine the history of those changes in conditions.

Biogeochemistry entails the study of a wide range of ecologic environments where minerals form. One must understand phase relations in...

- waters of lakes and oceans
- metals in hydrothermal ore deposits
- gases in volcanoes
- fluid phases and solid phases in magma
- soils (mineral solids, liquids, gases, and organics) in the regolith
- organic matter in sedimentary rocks

With basic knowledge from our studies of physical chemistry, it is possible to describe the nature of a mineral phase under certain physical and chemical conditions. The sub-disciplines that provide us with the tools to reconstruct the physical and chemical origins of geological systems include the fields of **thermodynamics, kinetics, and quantum mechanics.**

**Thermodynamics** is the study of energy and its transformations.

**Kinetics** is the study of rates of reactions.

**Quantum mechanics** helps us study the mechanisms of chemical reactions (i.e., reaction pathways).

Classical thermodynamics is based upon the equilibrium state. It is based upon the macroscopic (*i.e.*, little underlying knowledge of the crystal structure is required) measure of the *intensive* and *extensive* properties of phases in the system. Intensive properties can be specified at a particular point in the system. These properties are not “additive” in the sense that they do not require a specific quantity of sample, for the property to which they refer.

Included are;

- temperature
- density
- pressure
- solubility
- heat capacity
- viscosity
- melting/boiling point
- color
- resistivity

Extensive properties are additive by virtue of the fact that their values constitute a property of the whole system body. Included are:

- volume
- mass
- enthalpy (heat)
- energy (calories, joules)

Using empirically derived parameters that describe the chemical and physical state of matter, thermodynamics predicts the energy changes for any given transformation. In essence, it tells us the most stable state or set of phases that should be present, given certain pressure (P), temperature (T), and chemical conditions (X). PTX

Thermodynamics predicts what mineral assemblages should occur in a given environment assuming they are in chemical equilibrium.

The term **phase** is part of the system that is spatially uniform. We can use the term phase synonymously with **mineral** (if it is homogeneous at the atomic scale). A phase can be considered a solid, liquid, or gas with each having its own **stability region or field** in terms of chemical, pressure, and temperature conditions.

**Phase:** Physically distinct, mechanically separable, homogeneous. Phases are described by independent chemical species known as components.

*e.g.*, Quartz,  $\text{SiO}_2$  or Kyanite,  $\text{Al}_2\text{SiO}_5$

**Components** are the smallest number of chemical entities to define the composition of all phases in the a system.

*e.g.*, Si and  $\text{O}_2$  are components of quartz or  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  are components of Kyanite

**System** - a quantity of material defined by weights or numbers of molecules contained within a set of boundaries (i.e., imagine a container around the system, but the container is not part of the system). We generally classify systems into three conditions.

Isolated systems: This is an ideal situation where there is absolutely no transfer of energy or matter across the boundaries of the system.

Closed systems: In this case, there are possibilities for energy transfer but not matter. The matter can change in composition due to chemical reaction. We sometime assume this in certain geologic environments.

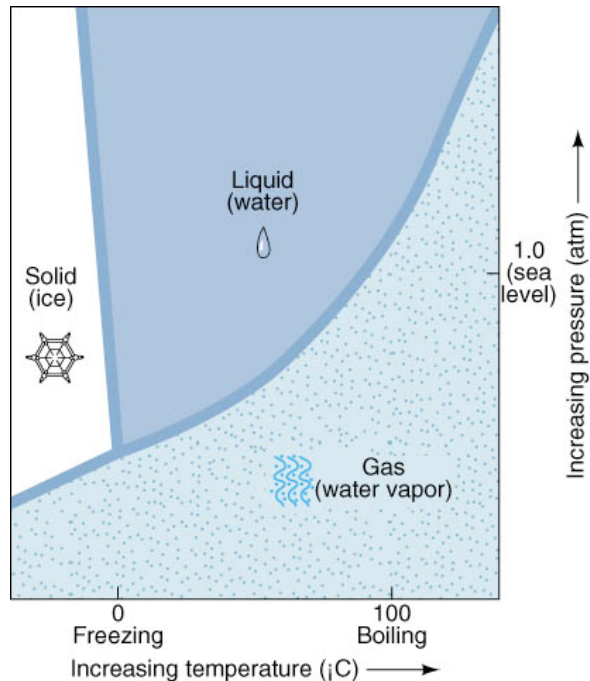
Open systems: Exchange of both energy and matter. This most often the rule in geologic environments.

### **Example of phase equilibria - $\text{H}_2\text{O}$**

Although thermodynamics tell us what reactions should take place, it does not tell us how fast a reaction will go.

**Unary systems.** Examples given are  $\text{H}_2\text{O}$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{SiO}_5$  where each can be considered a single component system with multiple phases at different temperature and pressure conditions.

Anatomy of a phase or stability diagram.



**Divariant area** - region where both T and P can be varied independently without changing the number of the phases present.

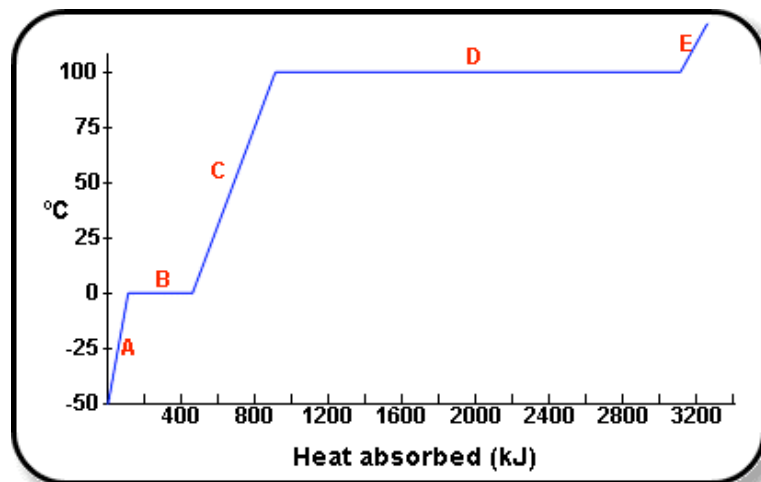
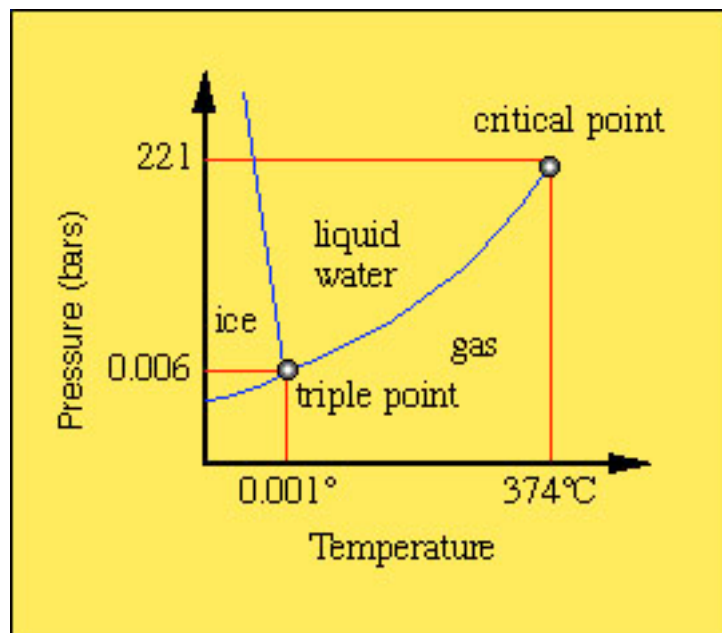
**Univariant curve** - loci of points (curve) where two phases coexist. Only T or P can be varied independently without changing the number of the phase present.

**Triple point** - The location where three phases can coexist. It is an invariant point where neither T, P nor any other intrinsic parameter can be changed without causing one phase to disappear.

The liquid-vapor curve extends to a point where the pressure is so great that the phase remains a liquid. So great that the fluid is often referred to as a supercritical fluid. The point in T - P space is termed the **Critical Point**.

**Metastability.** At each invariant point there is region where the univariant curve extends beyond slightly into a third phase region. The reason for this

condition is attributed to the additional energy that is required to nucleate a new phase. In the absence of nucleation energy, a metastable phase can persist into another stability region. A common example is super-cooled water (achieved by placing a bubble free container of distilled water in the freezer). When carefully removed from the freezer, a tap with a knife will cause instantaneous crystallization. This is referred to as the latent heat of crystallization and in the case of solid-gas transformation, the latent heat of vaporization.



Latent heat of vaporization for water.

## Gibbs phase rule

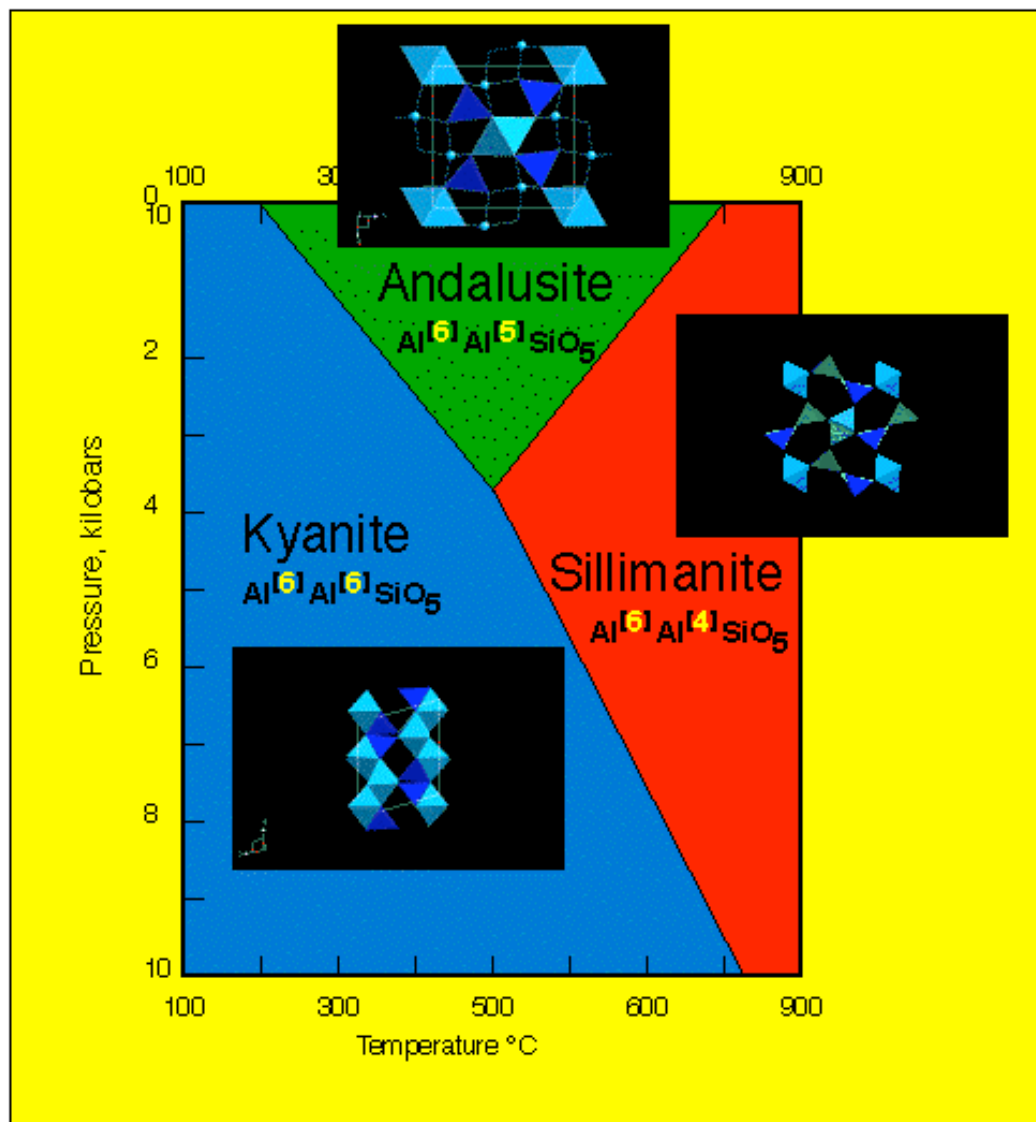
$$p + f = c + 2$$

where:

- $p$  = number of phases
- $f$  = the variance or number of degrees of freedom in the system
- $c$  = number of components

Example with the kyanite-sillimanite-andalusite series

Polymorphs of  $\text{Al}_2\text{SiO}_5$



$f$  is the number of variables that must be fixed to define a particular set of conditions in the system.

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In the case of the kyanite-sillimanite-andalusite series, like the  $H_2O$  system, there is a triple point or invariant point in T and P space. It is the unique set of T and P conditions under which all three phases can coexist.

This can be expressed by rearranging the Gibbs phase rule:

$$f = c - p + 2$$

In this case:

$$c = 1 \text{ (the component is } Al_2SiO_5\text{)}$$

$$p = 3 \text{ (there are three phases at this point)}$$

Therefore:

$$f = 1 - 3 + 2 = 0 \text{ (zero degrees of freedom)}$$

Along the curve or univariant line there is not one unique set of P and T conditions under which two phases can coexist.

In this case:

$$c = 1 \text{ (the component is } Al_2SiO_5\text{)}$$

$$p = 2 \text{ (there are two phases at this point)}$$

Therefore:

$$f = 1 - 2 + 2 = 1 \text{ (one degree of freedom)}$$

In the divariant or phase regions only one phase can coexist. No unique set of P and T conditions can be defined by the presence of one mineral phase

In this case:

$$c = 1 \text{ (the component is } Al_2SiO_5\text{)}$$

$$p = 1 \text{ (there is one phase at this point)}$$

Therefore:

$$f = 1 - 1 + 2 = 2 \text{ (two degrees of freedom)}$$

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**Binary Systems** are cases with two components in the system, meaning the system can be described by two chemical entities.

Binary systems are usually discussed in terms of temperature and the percentages of the components present (rather than grams of material) at a constant pressure (T-X diagrams).

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### **Examples of binary systems**

**Water and powdered glass** - two components ( $\text{H}_2\text{O}$ ,  $\text{SiO}_2$ ) , two phases - liquid and solid.

**Ice and powdered glass** - two components ( $\text{H}_2\text{O}$ ,  $\text{SiO}_2$ ) , two phases - both solid.

**Water and oil** - two components ( $\text{H}_2\text{O}$ , HC) , two phases - both liquids but are considered immiscible (no mixing at the molecular level).

**Water and alcohol** - two components ( $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ) , one phase - a miscible solution.

**Water (10 g) and Salt (1g)** - two components ( $\text{H}_2\text{O}$ , NaCl), one phase - a solution.

**Water (10 g) and Salt (10g)** - two components ( $\text{H}_2\text{O}$ , NaCl), two phases - a saturated solution and excess solid.

**Olivine - Forsterite/Fayalite series**- one phase - miscible solid solution (forsterite can occur with a small fayalite content or fayalite with a small forsterite content).

**Plagioclase - Albite/Anorthite series** - a partial solid-solution with a miscibility gap between the end-member (*i.e.*, homogeneous plagioclase).

**Albite - Silica** - Two immiscible solids.

## Mineral Assemblages

The study of mineral assemblages allows us to understand the conditions of rock formation, which in turn gives rise to insights to geologic process.

What is the first step in the study of a rock?

One usually begins by simply compiling a list the mineral assemblage and noting the textural relationships and relative abundances of each phase.

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**Example 1** Igneous mineral assemblage - rock type = *Granite*

[Quartz](#) - [Orthoclase](#) - [Albite](#) - [Biotite](#)

The chemical system\* can be described by  $\text{SiO}_2$  -  $\text{Al}_2\text{O}_3$  -  $\text{K}_2\text{O}$  -  $\text{Na}_2\text{O}$  -  $\text{FeO}$  -  $\text{MgO}$  -  $\text{H}_2\text{O}$

- Quartz -  $\text{SiO}_2$
- Orthoclase -  $2\text{KAlSi}_3\text{O}_8 = \text{K}_2\text{O} + 6\text{SiO}_2 + \text{Al}_2\text{O}_3$
- Albite -  $2\text{NaAlSi}_3\text{O}_8 = \text{Na}_2\text{O} + 6\text{SiO}_2 + \text{Al}_2\text{O}_3$
- Biotite -  $2\text{KMg}_2\text{FeSi}_3\text{AlO}_{10}(\text{OH})_2 = \text{K}_2\text{O} + 6\text{SiO}_2 + \text{Al}_2\text{O}_3 + 4\text{MgO} + 2\text{FeO} + 2\text{H}_2\text{O}$
- \*note: There are likely many other trace elements in a granite. We will only consider the major elements for now.

Relative to the wide range of chemical (X), temperature (T), and pressure (P) conditions that exist in the earth, if these minerals are texturally uniform (equal-granular), then they can be considered to have formed under very similar conditions (*i.e.*, all around the same time, within a small range of P-T-X conditions).

The sequence of events that lead to the formation of a mineral assemblage is termed **paragenesis**. It is assumed that the minerals present formed at or near the conditions of equilibrium (*i.e.*, in its stability field for a given set of P-T-X conditions).

In short - an assemblage consists of minerals that form under similar P-T-X conditions.

Recall Bowen's Reaction series from your introductory geology class.- Considered for a closed system case under isobaric conditions in a cooling magma.

Recall also that the melting and crystallization of a phase is related to

1. Polymerization of Si-O tetrahedra
2. Substitution of Al for Si in the tetrahedra
3. Nature of the metal cation compensating charge deficiency (*i.e.*, bond type)

Phase relations are further modified by composition of the system.

Geometry	Class	Si:O	Example
Isolated tetrahedra	<b>Nesosilicates</b>	1:4	Olivines
Two tetrahedra	<b>Sorosilicates</b>	2:7	Hemimorphite
Ringed tetrahedra	<b>Cyclosilicates</b>	1:3	Beryl
Single chain	<b>Inosilicate</b>	1:3	Pyroxenes
Double Chain	<b>Inosilicate</b>	4:11	Amphiboles
Sheet	<b>Phyllosilicates</b>	2:5	Micas, Clay Minerals
Framework	<b>Tectosilicates</b>	1:2	Quartz, Feldspars, Feldspathoids, Zeolites

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**Example 2** - Igneous mineral assemblage - rock type = *Basalt*

Plagioclase - Clinopyroxene - Orthopyroxene

The chemical system can be described by  $\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{Na}_2\text{O} - \text{FeO} - \text{MgO} - \text{CaO}$

- Plagioclase -  $\text{Na}_{0.5} \text{Ca}_{0.5} \text{Al}_{1.5} \text{Si}_{2.5} \text{O}_8$  -  $1/4 \text{Na}_2\text{O} + 1/2 \text{CaO} + 3/4 \text{Al}_2\text{O}_3 + 2.5\text{SiO}_2$
- Orthopyroxene - Hyperstene -  $\text{MgFeSi}_2\text{O}_6$  -  $\text{MgO} + \text{FeO} + 2\text{SiO}_2$
- Clinopyroxene - Diopside -  $\text{CaMgSi}_2\text{O}_6$  -  $\text{CaO} + \text{MgO} + 2\text{SiO}_2$

This mineral assemblage forms under **high temperature** (1000° to 1200° C) and **low pressure** (1-2 kilobars) conditions.

**Eclogite** - The same chemicals system  $\text{SiO}_2$  -  $\text{Al}_2\text{O}_3$  -  $\text{Na}_2\text{O}$  -  $\text{FeO}$  -  $\text{MgO}$  -  $\text{CaO}$  can be metamorphosed to a new assemblage under **lower temperature** (400° to 800° C) and **higher pressure** (12 to 30 kilobars) conditions.

- Kyanite -  $\text{Al}_2\text{SiO}_5$
- Pyrope -  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
- Grossular -  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
- Omphacite (Na-pyroxene or diopside with Jadeite component) ( $\text{Ca}$ ,  $\text{Mg}$ ,  $\text{Fe}$ )  $\text{Si}_2\text{O}_6$  (augite) +  $\text{NaAlSi}_2\text{O}_6$  (jadeite)

### Mineral Assemblages - low temperature

Let's reconsider the mineral assemblage found in a granitic rock.

[Quartz](#) - [Orthoclase](#) - [Albite](#) - [Biotite](#)

The chemical system can be described by  $\text{SiO}_2$  -  $\text{Al}_2\text{O}_3$  -  $\text{K}_2\text{O}$  -  $\text{Na}_2\text{O}$  -  $\text{FeO}$  -  $\text{MgO}$  -  $\text{H}_2\text{O}$  -  $\text{O}_2$  -  $\text{CO}_2$

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Upon close inspection, one might note that granites are often coated with other mineral products such as

- [Kaolinite](#) -  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
- Gibbsite -  $\text{Al}(\text{OH})_3$
- [Goethite](#) -  $\text{FeO}(\text{OH})$
- [Hematite](#) =  $\text{Fe}_2\text{O}_3$
- [Smectite](#) -  $\text{K}_{0.25} \text{Na}_{0.25} \text{Mg}_2\text{Al}_{0.5} \text{Si}_4\text{O}_{10}(\text{OH})_2 n\text{H}_2\text{O}$

Minerals formed under high P,T conditions are not stable near the earth's surface conditions in the presence of water, carbonic acid, and oxygen.

How do primary silicates weather? and why/how is this important to pollution problems or global climate change? This will be the subject of later discussions.

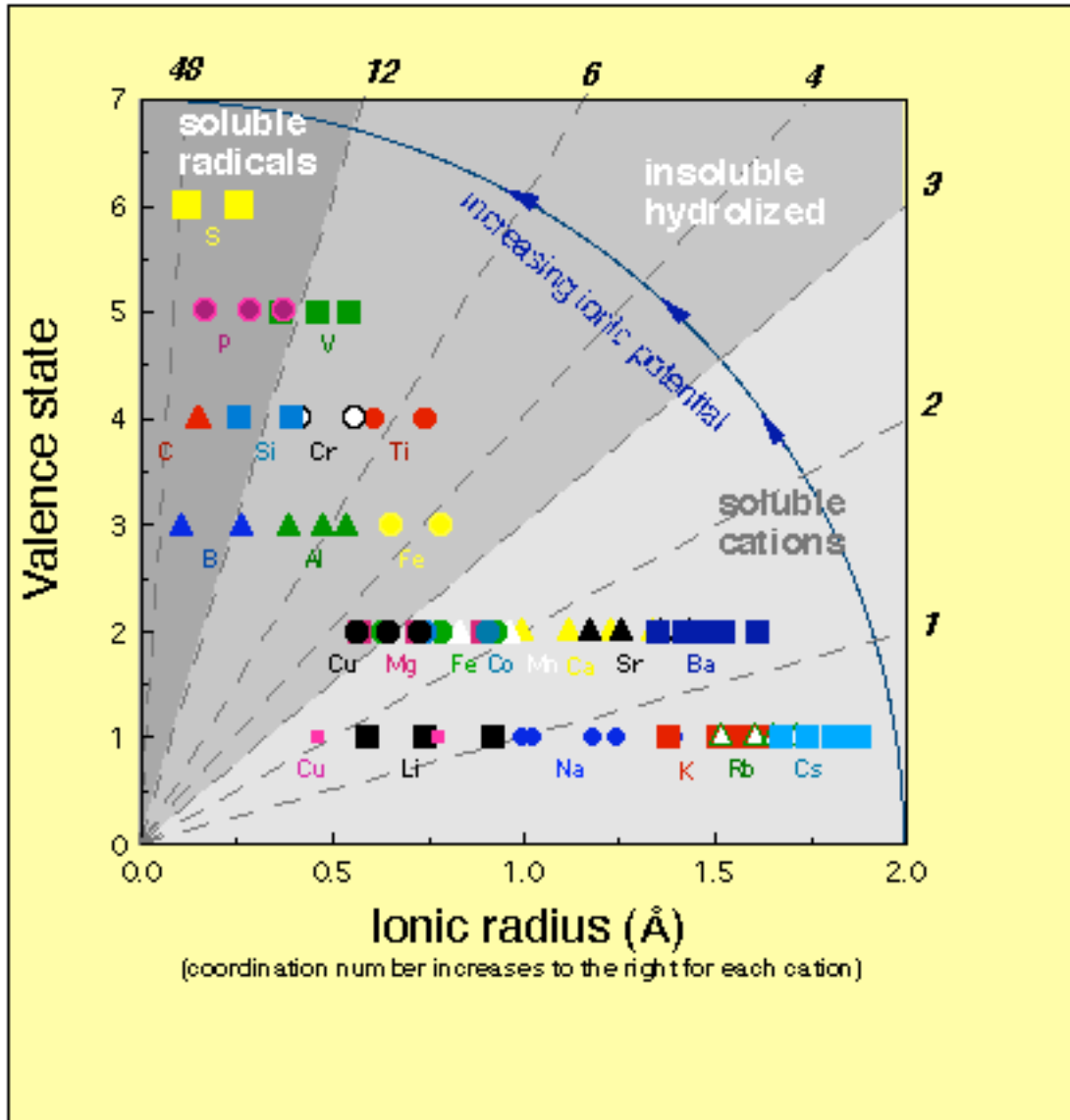
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## **Ionic Potential**

Mineral behavior near the earth's surface may be approached from the standpoint of the geochemical behavior of their constituent ions in dilute water solutions.

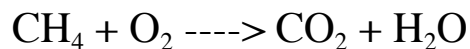
Behavior of an ion can be characterized by their ionic potential =  $\frac{\text{charge}}{\text{radius}}$

- Ionic potential > 3 - tend to be soluble in water
- Ionic potential 3 to 12 - tend to be insoluble in water
- Ionic potential > 12 tend to form soluble hydroxyl complexes



### Congruent versus incongruent dissolution

Analogy - burning of a hydrocarbon that can be represented by the reaction below.



The gases  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are colorless and odorless. But look at the flame!

Combustion is never complete - One sees soot, smoke and can smell methane. The reason is that there are partial reactions.

Similar **partial** reactions take place when weathering the primary silicates in a granite.

Reactions at surface conditions, (*i.e.*, weathering of minerals can be either congruent or incongruent).

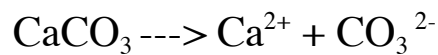
Attacking agents in mineral weathering:

- 1) acids (organic and inorganic)
- 2) dissolved oxygen
- 3) water

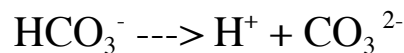
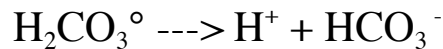
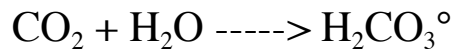
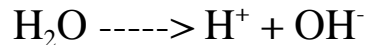
Because this is a water-dominated system the components in the system are defined by the solid phases, the liquid phase (water), and the dissolved species in the water.

### Congruent Reactions

Calcite dissolution/ppt



The calcite reaction is pH dependent (*i.e.* other components are in solution)

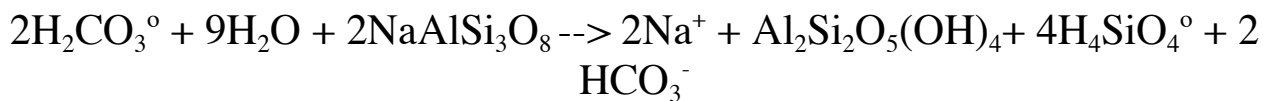


### Incongruent Reactions

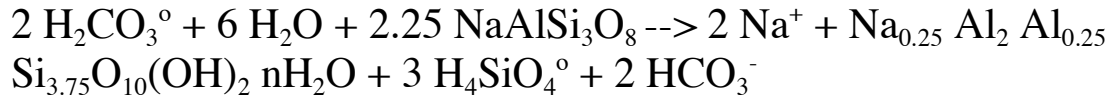
Gibbsite formation -  $\text{Al}(\text{OH})_3$



Kaolinite formation -  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$



Smectite formation -  $\text{Na}_{0.25} \text{Al}_2 \text{Al}_{0.25} \text{Si}_{3.75} \text{O}_{10}(\text{OH})_2 n\text{H}_2\text{O}$



Stability fields of alteration products (assuming equilibrium conditions).

Paragenesis is related to such factors as:

1. Initial composition , abundance and texture of primary silicates
2. Generation of acids (decomposition of organic matter by microbial activity)
3. Rainfall (i.e., flux of water)
4. Temperature of reaction

Balancing chemical reactions:

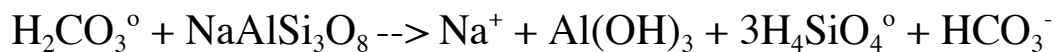
- 1) Conserve charge and mass
- 2) Assume species in reaction
- 3) Balance cations
- 4) Balance charge
- 5) Balance H<sup>+</sup>
- 6) Check oxygen

Example: Suppose you want to react carbonic acid and albite in an aqueous system and have gibbsite as the solid reaction product.



Clearly the above reaction is not mass balanced. So you must decide what aqueous species will be involved.

Assume bicarbonate, sodium, and silicon will be produced. The most common species under earth surface conditions are Na<sup>+</sup> , H<sub>4</sub>SiO<sub>4</sub><sup>°</sup> and HCO<sub>3</sub><sup>-</sup>



The above reaction is written to balance cations (and anions). Note also hydrogen (in the form of water) is needed. Below is the final balanced reaction.



